

A Chemotaxonomic Investigation of the Plant Families of *Apocynaceae*, *Loganiaceae* and *Rubiaceae* by their Indole Alkaloid Content

Inaugural-Dissertation
submitted for the
degree of Doctor of Philosophy
to the Philosophical Faculty, Section II
of the
University of Zürich

by
M. VOLKAN KISAKÜREK
of Istanbul (Turkey)

approved by
Prof. Dr. M. Hesse

Zürich 1980
Zentralstelle der Studentenschaft

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Prof. Dr. Manfred Hesse

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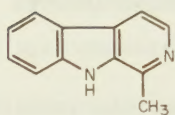
1. Introduction

The number of the structurally known indole alkaloids today amounts approximately to 1400. The indole alkaloids are defined as the natural organic products containing either the indole nucleus, or an oxidized, reduced or substituted equivalent of it [e.g. oxindole, pseudooxindole (ψ -indoxyl), dihydroindole, N-acyl-indole].

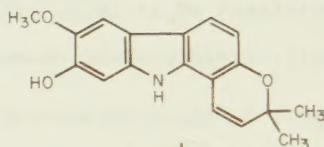
With respect to their structural features, the indole alkaloids can be divided into two main classes : the first one, being the simple indole alkaloids. They do not present a structural uniformity, having only the indole nucleus or a direct derivative of it as a common feature. Depending upon the constitution of the rest of the molecule, their occurrence is either distributed on many plant families (e.g. harmaline (aa), obtained from the families *Apocynaceae*, *Chenopodiaceae*, *Elaeagnaceae*, *Leguminosae*, *Loganiaceae*, *Passifloraceae*, *Polygonaceae*, *Rubiaceae*, *Symplocaceae*, and *Zygophyllaceae*) or restricted to very few or only one family (e.g. koenigine (ab) obtained only from *Rutaceae*) (scheme 1). Because of a relatively small number of the structurally known compounds, a chemotaxonomic examination of this heterogeneous class of plant bases seems to be irrelevant at the moment.

The indole bases of the second class contain two structure elements : tryptamine or tryptophan (ac, ad) with the indole nucleus and a C_9 - or C_{10} -monoterpene

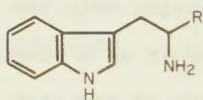
Scheme 1



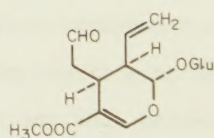
aa
harman



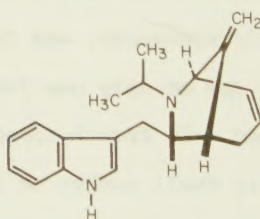
ab
koenigine



ac tryptamine R=H
ad tryptophan R=COOH



ae
(-)-secologanin



af
peduncularine

moiety, derived from secologanin (ae, scheme 1). Very probably, because of both of the common components and the biogenetic relationships, the occurrence of this second class of indole alkaloids is more specific and thereby suitable for comparative chemotaxonomic considerations.¹ Only the plumeran alkaloids hitherto were examined chemotaxonomically (2). In the course of the following study, the corynanthean-, vincosan-, vallesiachotaman-, strychnan-, aspidospermatan-, eburnan- and ibogan-alkaloids will be taken into consideration for a chemotaxonomic examination,^{2,3}

-
- 1) In the following study, we discuss only those C₉- or C₁₀-monoterpene indole alkaloids which are derived from secologanin (ae) or a biogenetic equivalent of it. The indole alkaloids recently isolated from *Aristotelia* species (*Elaeocarpaceae*) (e.g. peduncularine (af) (1)) were not considered for the purpose of this study, because the C₉- or C₁₀-monoterpene moiety they contain in addition to the tryptamine unit (ac) is not derived from secologanin.
 - 2) We attempted to consider the literature about alkaloid isolations up to the end of 1978. If any literature remained unmentioned, it happened without any intention.
 - 3) The following abbreviations will be used for the skeleton types of the alkaloids isolated : C = corynanthean, D = vincosan, V = vallesiachotaman, S = strychnan, A = aspidospermatan, E = eburnan, P = plumeran, J = ibogan.

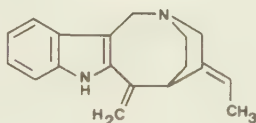
As mentioned, we considered only indole alkaloids with a C₉- or C₁₀-monoterpene moiety⁴ for the purpose of this study. The biogenetically related bases containing less than nine C-atoms (e.g. apparicine,

3) Cont'd.

The numbers after the abbreviations (e.g. C,D,V etc. are given to correspond to the number of the necessary operation steps (oxidation, bond formation, cyclisation, rotation followed by bond formation or cyclisation) to drive a certain skeleton variation starting from 1 (see part 2). The intermediary steps that haven't been isolated are designated only by numbers (e.g. 2a, 4a). In this way, these numbers correspond to the rank of "chemical complexity" for a given structure (according to this definition, for example, the skeleton type J7 should be regarded as "chemically more complex" than P4).

- 4) Also included are those alkaloids which contain additional C-atoms in their skeleton (e.g. strychnine; see part 2.4).

(ag) (3)) were not taken into consideration for our chemotaxonomic examination. We will not specially differentiate between alkaloid with or without a carboxy group in position 5 (fromad, e.g. 5 α -carboxy-tetrahydroalstonine (4) and tetrahydroalstonine (5a)) or a glycoside (e.g. 10- β -D-glucosyloxy-vincoside-lactam (6)).



ag, apparicine

On the basis of published papers (part 5), we considered approximately 1100 alkaloids obtained from 3450 isolations to study their biogenetic and chemotaxonomic relations. The corynanthean (C)-, vincosan (D)-, vallesiachotaman (V)-, strychnan (S)-, aspidospermatan (A)-, eburnan (E)-, plumeran (P)-, and ibogan (J)-alkaloids examined for the purpose of the following study were obtained from the plant species distributed among three plant families : *Apocynaceae*, *Loganiaceae* and *Rubiaceae*. Only a few alkaloids of the corynanthean-type were also detected in some species of *Alangiaceae*,⁵ *Ericaceae*,⁶

5) e.g. tubulosine (ah) from *Alangium lamareckii* Thw. (5)

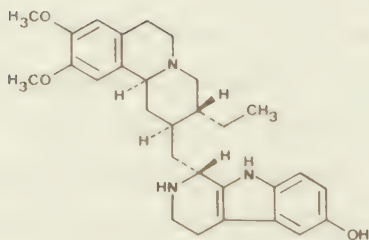
6) e.g. cannagunine B (ai) from *Vaccinium oxycoccus* (7)

and *Euphorbiaceae*⁷.

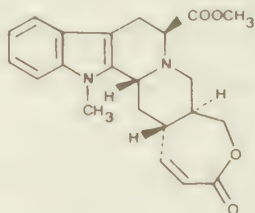
The mentioned sub-groups of indole alkaloids containing a C_9 - or C_{10} -monoterpene moiety isolated from the species of *Apocynaceae*, *Loganiaceae* and *Rubiaceae* will now be chemotaxonomically discussed with respect to their structure including the absolute configuration and the biogenetic relationships.

1.2. Assumptions and definitions

1. For the purposes of the following study, the papers were taken by us directly, i.e. without any further examinations of the published results regarding the



ah, tubulosine



ai, cannagunine B

7) e.g. yohimbine (see 2.1) from *Alchornea floribunda* Müll. Arg. (8).

botanical identification of the plant species and the physical data given for the determination of the isolated alkaloids.

2. The detection of a certain alkaloid from the same plant source reported by different authors is considered as only one isolation.
3. The bisindole alkaloids are also taken into consideration, either as one or two isolations, according as they contain one or two units respectively of the skeleton type which is being discussed.
4. The natural indole bases occurring with (+)- and (+)- or (-)- $[\alpha]_D$ -values have been regarded as two distinct alkaloids.
5. In addition to the structural and chemical characteristics, the absolute configuration of the alkaloid was considered as a further criterion for the chemotaxonomy. Unfortunately, we could use only ca. 46% of alkaloid isolations in this respect, since the necessary indications were completely or partly neglected in the original papers. In these cases, the absolute configurations are still unknown.

In most cases, the alkaloids examined have several chiral centers that are partly interdependent. In contrast to the common expression, we used the letters α and β to designate the absolute configurations. The conventional

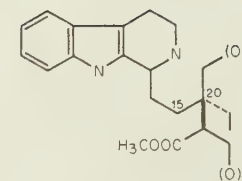
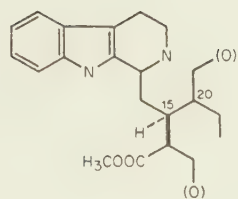
R,S-nomenclature could not be used for the considerations of our study, since different substitutions by the same absolute configuration would have led to the alteration of priorities resulting on the reverse R,S-expression. The absolute configurations of the alkaloid groups taken into consideration in this study were defined on the basis of biogenetic correlations as shown in scheme 2.

6. The names of the plant species were checked, in some cases corrected and replaced if registered under synonymous names in the papers.
7. In the course of this study, the so-called plumeran-alkaloids were taken into consideration so far as they should be regarded for a chemotaxonomic evaluation of the indol alkaloids with a C₉- of C₁₀-monoterpene moiety. (For further details, ref.2 is recommended). Also in this case, we considered the literature till the end of 1978.
8. The numbering of the atoms of the various alkaloid skeletons was done according to the biogenetic method.
9. The botanical classification of the three mentioned plant families accepted by Leeuwenberg (9) is given in Table 1. Only those genera are indicated (in alphabetical order) who contain indole alkaloids under discussion.

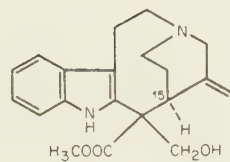
Scheme 2.⁸ α -Configurations of the indole alkaloids
with a C₉- or a C₁₀ monoterpene moiety.

8) If not given otherwise, the structures given in this scheme represent the skeleton types and not the complete constitutions. Therefore, we partly omitted the N-substituents and generally showed the chirality assignment only on C-15 or its equivalents. Also, the oxidation state of the single C-atoms is not always shown correctly.

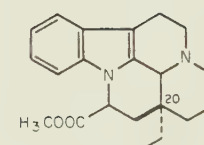
Corynanthean-,
Vincosan-,
Vallesiachotaman-types



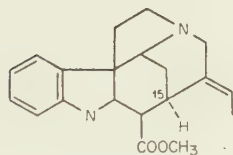
Stemmadenine



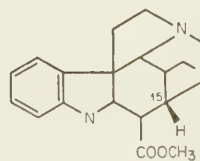
Eburnan-type



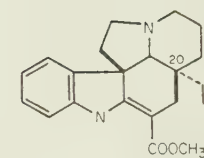
Strychnan-type



Aspidospermatan-type



Plumeran-type



Ibogan-type

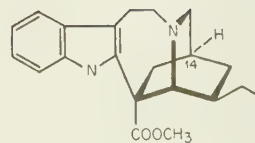


Table 1. The botanical classification of the plant

families APOCYNACEAE, LOGANIACEAE and RUBIACEAE

(Only those genera are given which contain indole
alkaloids)

Family : APOCYNACEAE

Subfamily : Plumerioideae

Tribe : *CARISSEAE*

Carpodinus, Hunteria, Melodinus,
Picralima, Pleiocarpa, Polyadoa

Tribe : *TABERNAEMONTANEAE*

Anacampta, Bonafousia, Callichilia, Capuronetta,
Conopharyngia, Crioceras, Ervatamia, Gabunia,
Hazunta, Hedranthera, Muntafara, Pagiantha,
Pandaca, Peschiera, Phrissocarpus, Rejoua,
Schizozygia, Stemmadenia, Stenosolen, Tabernaemontana,
Tabernanthe, Voacanga

Tribe : *ALSTONIEAE*

Alstonia, Ammocallis, Amsonia, Aspidosperma,
Catharanthus, Craspidospermum, Diplorrhynchus,
Geissospermum, Gonioma, Haplophyton, Plumeria,
Rhazya, Tonduzia, Vinca

Table 1. Cont'd

Tribe : *RAUVOLFIEAE*

Bleekeria, Cabucala, Excavatia, Kopsia,
Lochnera, Neisosperma, Ochrosia, Rauvolfia,
Vallesia

Family : *LOGANIACEAE*

Tribe : *GELSEMIEAE*

Gelsemium, Mostuea

Tribe : *STRYCHNEAE*

Gardneria, Strychnos

Family : *RUBIACEAE*

Subfamily : *Rubioideae*

Tribe : *PSYCHOTRIEAE*

Palicourea

Tribe : *UROPHYLLEAE*

Pauridiantha

Subfamily : *Cinchonoideae*

Tribe : *NAUCLEEAE*

Adina, Anthocephalus, Cephalanthus, Mitragyna,
Nauclea, Neonauclea, Sarcocephalus, Uncaria

Tribe : *CINCHONEAE*

Cinchona, Corynanthe, Pausinystalia, Remijia

Tribe : *MUSSANDEAE*

Isertia

Table 1. Cont'd

Subfamily : Guettardoideae

Tribe : GUETTARDEAE

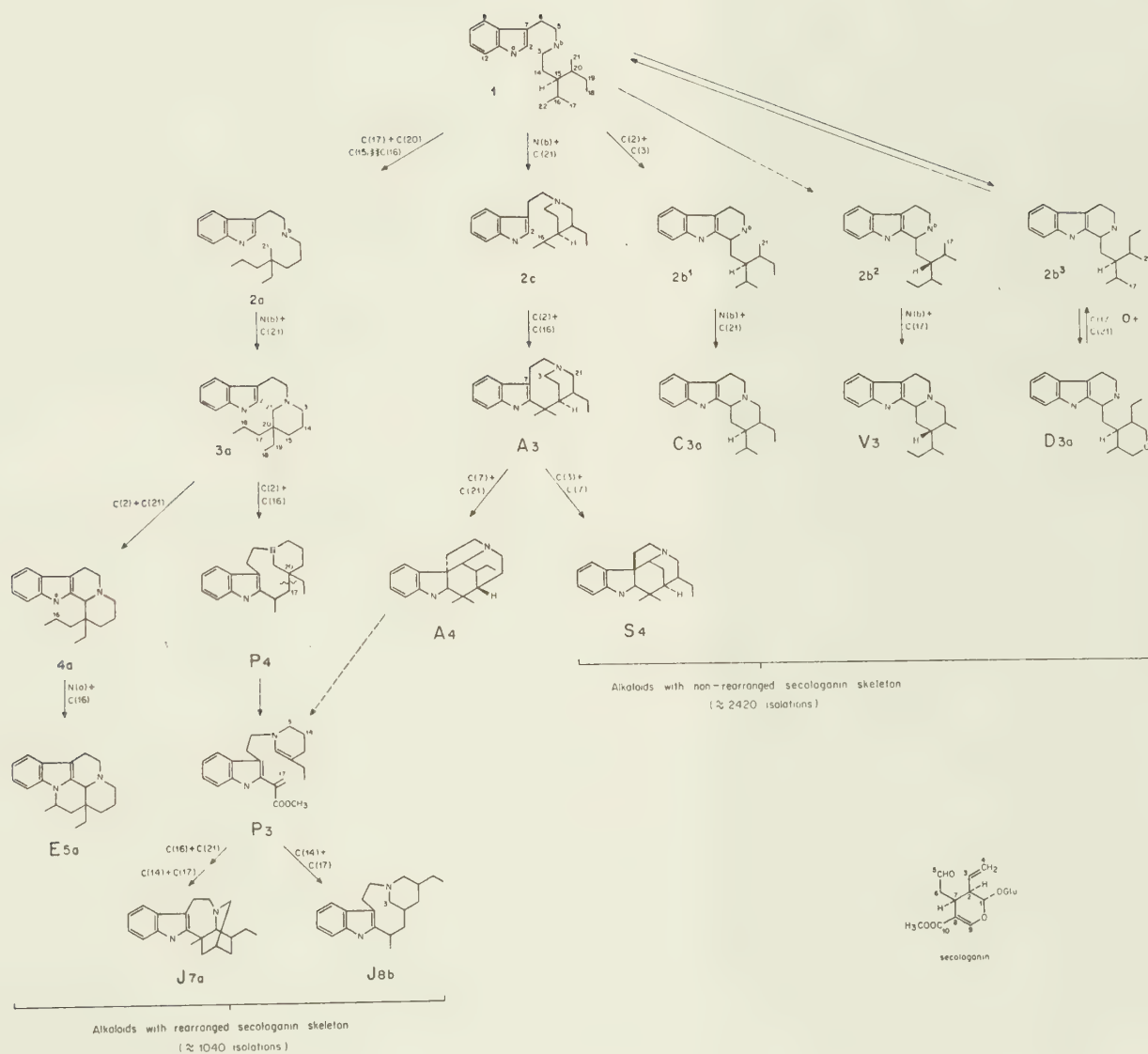
Antirhea, Guettarda

2. Skeleton types of the indole alkaloids and their botanical occurrence

The indole alkaloids with a C_9 - or C_{10} - monoterpene moiety, as mentioned before, are classified into the following subgroups : corynanthean (C)-, vincosan (D)-, vallesiachotaman (V)-, strychnan (S)-, aspidospermatan (A)-, eburnan (E)-, plumeran (P)-, and ibogan (J)-types. In a simplified manner, the biogenetic relationships of these main skeleton types are demonstrated in Scheme 3: As an established fact (10) D3a is obtained from condensation of tryptamine (ac) (or in some cases tryptophane (ad) with secologanin (ae). All of the main skeleton types can be derived from D3a. Skeleton D3a can be converted to 1 by opening of the C(17)-O-C(21)-bond via 2b³. From 1, 2b¹, 2b², 2b³ and 2c can be obtained without rearrangement, on the one hand, and on the other hand 2a with a rearrangement of the secologanin part. The ring formation between C(2) and C(3) leads to 2b. 2b¹, 2b², and 2b³ differ from each other through rotation around the C(14)-C(15)- and C(15)-C(16)-bonds respectively. Ring closures between C(21) and N(b) respectively C(17) and N(b) in 2b¹ and 2b² give rise to the main skeleton of corynanthean-type C3a and respectively main skeleton of vallesiachotaman-type V3. A new additional

Scheme 3.⁹ Biogenetic relationships of the eight main
skeleton types (C, D, V, S, A, E, P and J) of
indole alkaloids with a C₉- or C₁₀-monoterpene
moiety

-
- 9) The numbers after the abbreviations (e.g. C, S, J, etc. are given to correspond to the numbers of the necessary operation steps (oxidation, bond-formation, cyclisation, rotation followed by bond formation or cyclisation) to derive a certain skeleton, variation starting from 1. The intermediary steps that haven't been isolated are designated only by numbers (e.g. 2a, 4a). In this way, these numbers correspond to the rank of "chemical complexity" for a given structure (according to this definition, for example, the skeleton type J7 should be regarded a "chemically more complex" than P4.)



bond between C(17)-OH and C(21) in 2b³ yields the main skeleton of vincosan-group D3a. 2c is obtained by ring closure between C(21) and N(b) in 1. An additional ring closure between C(16) and C(2) in 2c yields A3, the main skeleton of aspidospermatan group. Starting with A3, S4 is obtained through another ring formation between C(3) and C(7) on the one hand, and on the other hand ringclosure between C(21) and C(7) yields A4. Besides the biogenetic pathways as demonstrated in scheme 2, there have been other conceivable proposals (11, 12, 13, 14).

2a is derived from 1 by cleavage of the bond C(15)-C(16) followed by the formation of a new bond C(17)-C(20). Ring closure between C(21) and N(b) leads to 3a from which 4a and main skeleton of plumeran group P4 can be derived by additional ring closures [C(2)-C(21)] and respectively [C(2)-C(16)]. Ring closure [N(a)-C(16)] in 4a yields E5a, the main skeleton of eburnan group. The cleavage of the bond C(17)-C(20) in P4 forms P3. By further reactions, the main skeletons of ibogan group J7a and J7b can be derived from P3.

Further reactions are necessary to form starting from C3a, D3, V3, S4, A4, E5a, P4 and J7a derivatives of various skeleton types.

2.1. Alkaloids of corynanthean (C)-type

In scheme 4, the skeleton types of the corynanthean group - which presents the most extensive class of indole alkaloids - are given according to their botanical occurrences in plant families. Only 26 of the 41 skeleton variations were depicted to simplify the presentation of structural features. 15 variations which were omitted in scheme 4 were distributed according to their structural relations among 26 skeletons occurring in the same plant families. Those skeleton types that include further variations omitted in the scheme are given in brackets underneath the main type. Table 2 offers an outline of all the skeleton types including examples of variations and all of the corresponding alkaloids represented by a specific skeleton type.

Scheme 4.¹⁰ Distribution of alkaloids of corynanthean (C)-
type in plant families

-
- 10) In schemes 4, the skeleton types are demonstrated according to their occurrence in plant families. In the middle of the scheme (circle), the skeletons are given of which alkaloids were detected in all of three plant families : Apocynaceae, Loganiaceae and Rubiaceae. Outside of the circle in separate regions, the skeleton types are included occurring in only one or two plant families. The thickness of the arrows are chosen to correspond proportionally to the abundance of the alkaloids of a certain skeleton type placed at their heads. The direction of the arrows are in agreement with biogenetic considerations. The numbers in brackets indicate that certain types include further derivable variations (e.g. C4e includes also C5g which is not given in the scheme, for purpose of simplification. For those further variations, see Table 2 and Table 3).

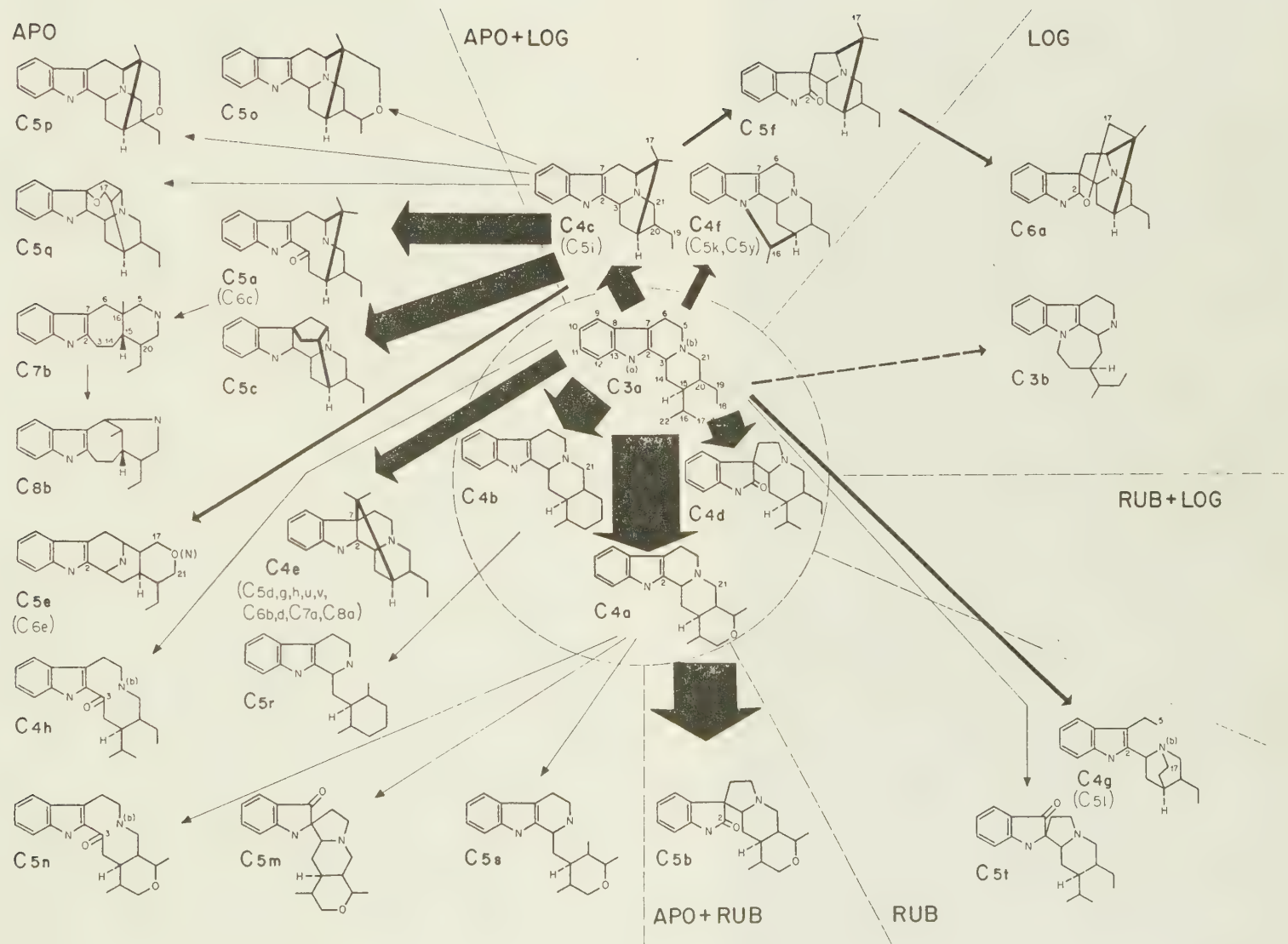


Table 2. Corynanthean (C)-type - examples ofstructure and names of all isolated alkaloids

(° = bisindole alkaloids, given twice if necessary)

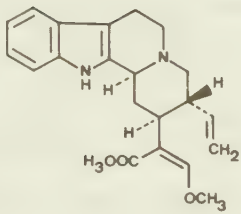
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C3a</u>	 corynantheine	adirubine (anhydro-a.), alkaloid-numbers : II/296, II/298, II/328, III/352, III/354, III/382, III/384, IV/354, IV/356, IV/384, IV/386, angusteine, aspexcine, corynantheal, corynantheidine (iso-c.), corynantheine (c.-aldehyd; dihydro-c.; dihydro-c.-N-oxide, epi-allo-c.), corynantheol (18,19-dihydro-c.; dihydro-c.-methochloride; 10-methoxy-c.-β-methochloride; 10-methoxy-dihydro-c.), diploceline, flavocarpine, gambirine, geissoschizal, geissoschizine (decarbo-methoxy-g.; g.-methylether), geissoschizol (10-hydroxy-g.; 10-methoxy-g.), geissospermine°, hervine, hirsuteine, hirsutine (h.-N-oxide), huntrabrine-methochloride, isostrychnopentamine A, isostrychnopentamine B, methoxy-geissoschizoline, mitraciliatine, ochrolifuanine A (o.- B; o.-N-oxide; 3-dehydro-o.; hydroxy-o.), ochromianine, ochropposinine, ochrosandwine, paynantheine (iso-p.), serpentinine°, sitsirikine (dihydro-s.; 16-epi-s.; iso-s.; specio-ciliatine, speciogynine, strychnobaridine, strychnopentamine, tschibangensine, usambarensine (3',4'-dihydro-u.; N_(b)-methyl-3',4'-

Table 2. Cont'd

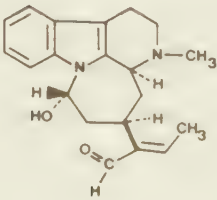
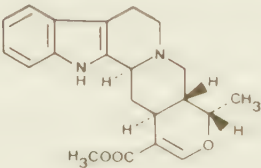
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C3a</u>	(cont'd)	
	dihydro-u.; N'-methyl-u.), usambaridine (u.-Br; u.-Vi; 18,19-dihydro-u.-Br; 18,19-dihydro-u.-Vi), usambarine (18,19-dihydro-u.)	
<u>C3b</u>	 akagerine	akagerine (17-O-methyl-a.), kri-bine (epi-21-O-methyl-k.; 21-O-methyl-k.).
<u>C4a</u>	 ajmalicine	ajmalicine (10,11-dimethoxy-a.; 19-epi-a.; 3-iso-a.; 3-iso-19-epi-a.), ajmalicinine (10,11-dimethoxy-a.), akuammigine (4R-a.-N-oxide; 4S-a.-N-oxide), alkaloid numbers : I/352; I/382a; I/382b;
	alstonine, aricine, bleekeringine, cabucine, cabucinine, cathenamine, ervine, herbacine, herbaine, holeinine, melionine A (m.-B), mitrajavine, raufloridine, raumitorine, rauniticine (3-iso-r.), raunitidine, rauvanine, reserpiline (19,20-dehydro-r.; iso-r.;	

Table 2. Cont'd

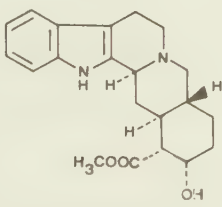
Type	Example	Alkaloids
<u>C4a</u> cont'd		
		r.-methosalt), reserpine (iso-r.), roxburghine (r.- A; r.- B; r.- C; r.- D; r.- E), serpentine (19-epi-s.; 10-methoxy-s.), serpentinine ^o , tetrahydro-alstonine (5 α -carboxy-t.; 4R-t.-N-oxide), tetraphylline, tetraphyllinine.
<u>C4b</u>		alloyohimbine, alstoniline, anhydro-alstonatine, canembine, corynanthine (5 α -carboxy-c.), 3,4-dehydro-alstovenine, deserpidine, deserpidine, excelsinine, gambirtannine (decarbomethoxy-
	yohimbine	dihydro-g.; dihydro-g.; neooxy-g.; oxo-g.), isorauhimbine, melinonine E, methyl deserpidate, methyl reserpate, ourouparine, poweridine, pseudoreserpine (iso-p.), pseudoyohimbine (11-methoxy-p.), quaternatine, raugustine, raujemidine, raunescine (iso-r.), renoxydine, rescidine, rescinnamine, reserpine (iso-r.), sempervirine, seredine, venenatine (iso-v.), veneserpine, venoxidine, yohimbine (O-acetyl-y.; 19,20-dehydro-y.; 18-hydroxy-y.; 11-methoxy-y.), 3,4,5,6-tetradehydro- β -yohimbinium-chloride, α -yohimbine, β -yohimbine, yohimbol-methochloride.

Table 2. Cont'd

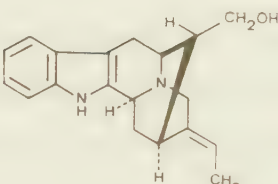
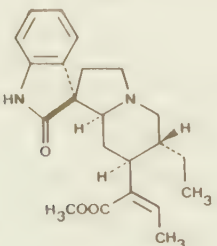
Type	Example	Alkaloids
C4c	 normacusine B	affinisine, akuammidine (a.-metho- salt; deformat-a.; N_(b)-methyl-a.- chloride; N_(a)-methyl-10-methoxy-a. N_(b)-methyl-10-methoxy-a.), O-benzo- tombozine, ervincidine, gardnerine geissolosimine^o, lochneram, lochne- rine, lochvinerine, macralstonidine^o, macusine A, macusine B (O- methyl-dihydro-m.; O-methyl-m.; O-methyl-nor-m.; O-methyl-nor-m.-B-N- oxide; nor-m.), macusine C, majvinine, pericyclivine, polyneuri- dine (O-acetyl-p.), sarpagine (N_(a), N_(b)-dimethyl-s.-chloride; N_(a)-methyl-s.; neo-s.), spegatrine, vellosimine (10-methoxy-v.), voachalotine (17-O-acetyl-19,20-dihydro-v.; 3-hydroxy-v.; 21- hydroxy-v.).
C4d	 rhynchophylline	ciliaphylline (c.-N-oxide), cory- noxine (iso-c.), corynoxine A (c.-B), mitrafoline (iso-m.), mitra- gynine (m.-oxindol A; m.-oxindol B) ochromianoxine, rhynchociline (r.- N-oxide), rotundifoline (iso-r.), rhynchophylline (anti-iso-r.-N- oxide; iso-r.; iso-r.-N-oxide; r.-N-oxide), rotundifoline (anti-r-

Table 2. Cont'd

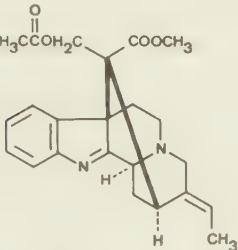
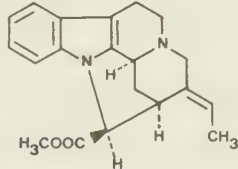
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C4d</u> cont'd		
		N-oxide; 3-epi-iso-r.; iso-r.), speciofoline (iso-s.), specio- noxine (iso-s.), stychnofoline (iso-s.), strychnophylline (iso-s.).
<u>C4e</u>	 akuammiline	akuammiline (desacetyl-a.; des- acetyl-deformo-a.; 10-methoxy- desacetyl-a.), cabucraline, catha- foline, pleiocraline°, quaternoxine, raufloricine, rhazinaline, strictalamine, strictamine, um- bellamine°.
<u>C4f</u>	 pleiocarpamine	macralstonine°, macrocarpamine°, C-mavacurine, pleiocarpamine (2,7- dihydro-p.; p.-methochloride), pleio- corine°, pleiocraline°, pleioxmutinine°, C- profluorocurine, pycnanthine° (14',15'-dihydro-p.°), pycnanthi- nine°, villalstonine°.

Table 2. Cont'd

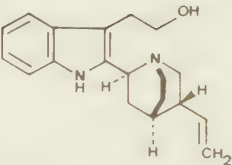
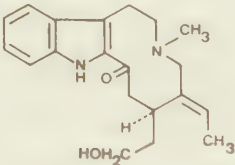
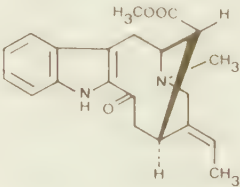
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C4g</u>	 cinchonamine	cinchonamine, cinchophyllamine (iso-c.).
<u>C4h</u>	 burnamicine	burnamicine.
<u>C5a</u>	 vobasine	accedinine (N-demethyl-16-epi-a.), accedinine°, accedinisine°, affi- nine, capuvosidine°, capuvosine° (15-dehydroxy-c.; N-demethyl-c.). conoduramine° (19,20-epoxy-c.), conodurine° (19-oxo-c.), dregamine, 16-epi-affinine, 16-epi-vobasinicacid, gabunamine°, gabunine°,

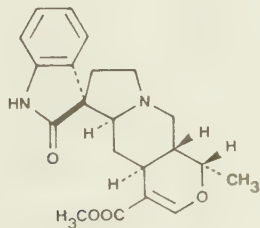
Table 2. Cont'd

Type	Example	Alkaloids
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C5a	cont'd	
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N-methyl-16-epi-affinine, ochropamine, ochropine, pelirine, periformyline, perivine, tabernaelegantine A° (t.-B; t.-C; t.-D), tabernaelegantinine A° (t.-B), voacarpine, tabernaemontanine, vincadifline, voacamidine°, voacamine° (16-decarbomethoxy-dihydro-v., 16-decarbomethoxy-20'-epi-dihydro-v.; 18'-decabomethoxy-v.; N-demethyl-v.; v.-N-oxide), voacorine° (19-epi-v.), vobasine (16-decarbomethoxy-19,20-dihydro-v.).

C5b		
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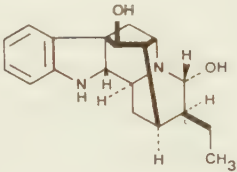


mitraphylline

alkaloid V, caboxine A (iso-c.-A), carapanaubine (c.-N-oxide; iso-c.), elegantissine (iso.-e.), ericinine, formosanine (iso-f.), gambirdine (iso-g.), majdine (iso-m.), herba-
line, herboxine, isocaboxine B, javaphylline, mitraphylline (10,11-

dimethoxy-iso-m.; iso-m.; iso-m.-N-oxide; m.-N-oxide), rauvoxine, rauvoxinine, speciophylline (s.-N-oxide), uncarine F (uF-N-oxide), vineridine (v.-N-oxide), vinerine (N-acetyl-v.; v.-N-oxide), vinerinine, pteropodine (iso-p.; iso-p.-N-oxide; p.-N-oxide).

Table 2. Cont'd

Type	Example	Alkaloids
<u>C5c</u>		ajmalidine, ajmaline (17-acetyl-a.; 1-demethyl-17-O-acetyl-21-desoxy- a.-diene (1,19); diacetyl-a.; iso-a.; 12-methoxy-a.; nor-a.; 17-O- (3',4',5')-trimethoxybenzoyl-a.), alstonisidine°, endolobine, herba-
	ajmaline	

dine, herbamine, indolenine RG, majoridine, mauisensine, mitoridine (nor-m.), purpeline (N_(a)-demethyl-dihydro-p.; N_(a)-demethyl-p.; dihydro-nor-p.; nor-p.) quebrachidine, raucaffricine, rauflorine, rauvomitine (N_(a)-demethyl-r.), reflexine, sandwicine (iso-s.), seredamine (N_(a)-demethyl-s.; nor-s.; 17-O-trimethoxybenzoyl-s.), tetraphyllicine (dimethoxy-t.; 10-hydroxy-nor-t.; monomethoxy-t.; nor-t.; trimethoxy-t.), vincamajine, (O-benzoyl-v.; 10-methoxy-v.; O-3,4,5-trimethoxybenzoyl-hydroxy-v.; O-3,4,5-trimethoxybenzoyl-v., O-3,4,5-trimethoxycinnamoyl-10-hydroxy-v.; O-3,4,5-trimethoxycinnamoyl-10-methoxy-v.; O-3,4,5-trimethoxy-cinnamoyl-v.), vincamajoreine, vincamedine, vincarine, vinorine (10-methoxy-v.), vomalidine, vomilenine.

Table 2, Cont'd

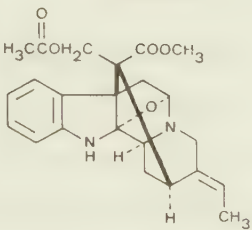
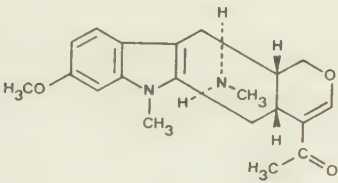
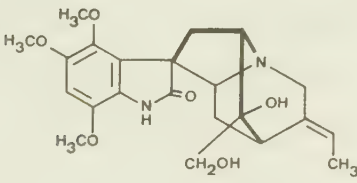
Type	Example	Alkaloids
C5d	 picraline	picralinal, picraline (desacetyl-p.), picralstonine, picrinine, quaternidine, quaternine, vincaricine, vincaridine, vincarinine.
C5e	 alstophylline	alstonerine, alstonisidine°, alstophylline, macralstonidine°, macralstonine° (N' (a)-demethyl-anhydro-m.), macrocarpine°, suaveoline, talcarpine, villalstonine°.
C5f	 chitosenine	alkaloid I (a.-J; a.-L; a.-M; a.-N), chitosenine, gardmultine°, voachalotine-oxindole.

Table 2. Cont'd

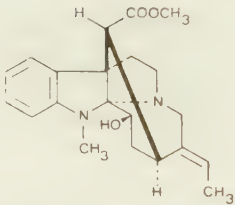
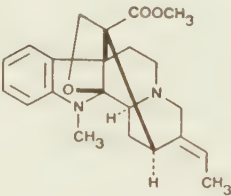
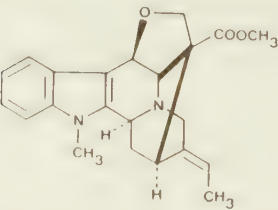
Type	Example	Alkaloids
<u>C5g</u>	 deformsine	pleiocorine ^o , cabuamine (deformo-c.), deformsine, echitamine (nor-e.), 3-epi-3,17-dihydro-deformsine, vincoridine, vincorine,
<u>C5h</u>	 pseudoakuammigine	akuammigine (O-methyl-a.), pseudoakuammigine.
<u>C5i</u>	 dehydrovoachalotine	dehydrovoachalotine, gardnutine (18-hydroxy-g.).

Table 2. Cont'd

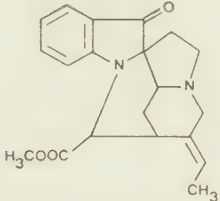
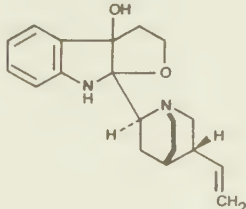
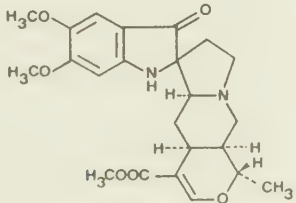
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C5k</u>	 fluorocarpamine	fluorocarpamine, C-fluoro-curine.
<u>C5l</u>	 quinamine	conquinamine, quinamine.
<u>C5m</u>	 isoreserpiline-pseudoindoxyl	isoreserpiline-pseudoindoxyl.

Table 2. Cont'd

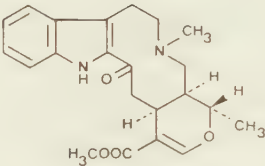
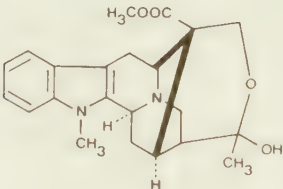
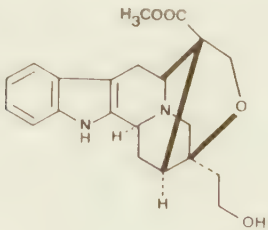
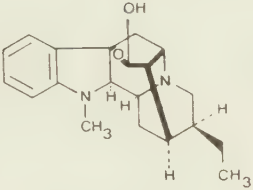
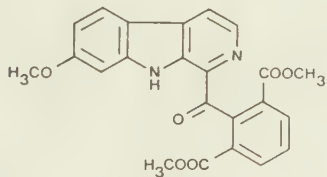
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C5n</u>		picraphylline (10,11-dimethoxy-p.; 20-epi-p.).
<u>C5o</u>		talpinine, voacoline.
<u>C5p</u>		eburnaphylline.
	eburnaphylline	

Table 2. Cont'd

Type	Example	Alkaloids
<u>C5g</u>		rauwolfinine.

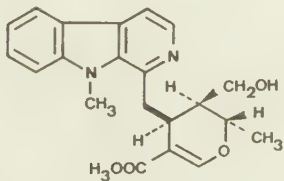
rauwolfinine

<u>C5r</u>		alstonilidine.
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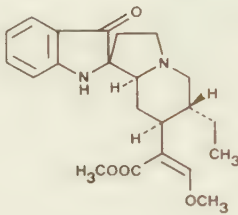
alstonilidine

<u>C5s</u>		alstonidine.
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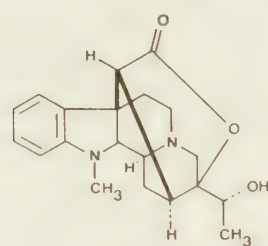


alstonidine

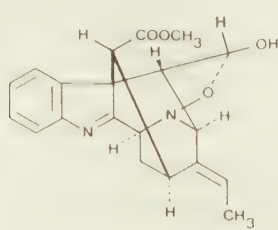
Table 2. Cont'd

<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C5t</u>		dihydro-corynantheine- pseudoindoxyl.

dihydro-corynantheine-pseudoindoxyl

<u>C5u</u>		quaternoline.
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quaternoline

<u>C5v</u>		nareline.
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nareline

Table 2. Cont'd

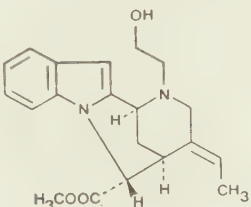
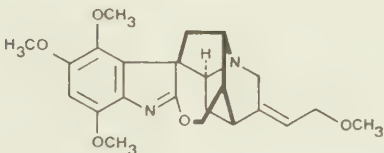
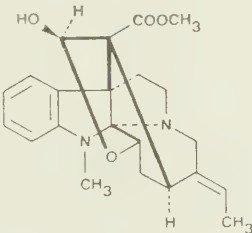
Type	Example	Alkaloids
<u>C5y</u>	 vinoxetine	vinoxetine.
<u>C6a</u>	 gardneramine	gardfloramine (18-demethox-g.); gardmultine°, gardneramine (18-demethoxy-g.; 18-demethyl-g.; g.-N-oxide).
<u>C6b</u>	 corymine	corymine (acetyl-c.).

Table 2. Cont'd

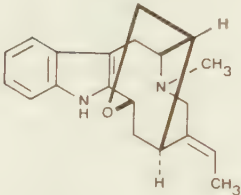
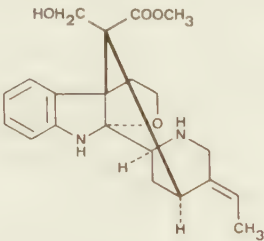
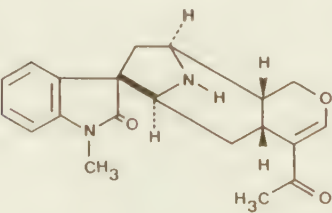
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C6c</u>	 anhydro-vobasine-diol	anhydro-vobasine-diol.
<u>C6d</u>	 aspidodasycarpine	aspidodasycarpine, lanciferine (10-hydroxy-1.; 10-methoxy-1.), lonicerine.
<u>C6e</u>	 alstonisine	alstonisine.

Table 2. Cont'd

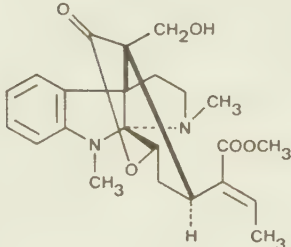
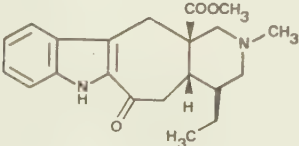
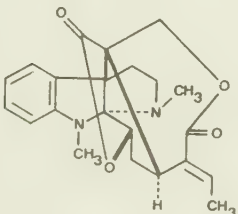
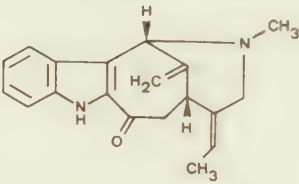
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C7a</u>	 eripine	eripine.
<u>C7b</u>	 ervatamine	ervatamine (19-dehydro-e.; 20-epi-e.), methuenine.
<u>C8a</u>	 erinine	erinicine, erinine, isocorymine.

Table 2. Cont'd

<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>C8b</u>		ervitsine.

ervitsine

The biogenetic relationships of C-skeleton types can be explained as follows : Starting with C3a (e.g. corynantheine¹¹), several ring closures can take place resulting in formation of the main variations : a new bond between C(17) and C(18) leads to C4b (e.g. yohimbine), reaction of C(17)-OH with C(19) forms C4a (e.g. ajmalicine), combination of C(16) with N(a) results in C4f (e.g. pleiocarpamine), C(16) + C(5) → C4c (e.g. normacusine B), C(16) + C(7) → C4e (e.g. akuammiline). These main skeleton types can undergo further reactions : starting with C3a, ring closure [C(17) + N(b)] followed by ring opening [N(b)-C(5)] gives C4g (e.g. cinchonamine); from C4c ring closure [C(17)-OH+C(21)] followed by ring opening [N(b)-C(21)] yields C5e (e.g. alstophylline). For the corynanthean group of skeleton types, oxidational process seem to be characteristic, involving especially the carbon-atoms 2, 3 and 7.

The C(2)-oxidations under rearrangement of the skeleton produce alkaloids containing the oxindol chromophore = C3a → C4d (e.g. rhynchophylline), C4a → C5b (e.g. mitraphylline),

11) Specific alkaloid-examples of skeleton types are illustrated in table 2.

C4c → C5f (e.g. chitosenine), and C5e → C6e (e.g. alstonisine). By oxidation on C(3) are formed : C5a (e.g. vobasine) from C4c, C4h (e.g. burnamicine) from C3a, C5n (e.g. picraphylline) from C4a, and C5g (e.g. deformo-corymine) from C4e. (In order to obtain C5g from C4e, a ring closure [C(2)-N(b)] takes place in addition to the cleavage of the bond N(b)-C(3)). In all of the cases given for C(3)-oxidations, the bond N(b)-C(3) is to be recognized as cleaved, only if N(b) is tertiary so that a transannular interaction with C(3)=O-group (or C(3)-OH-group) in the ten-membered ring could be neglected. The oxidation on C(7), comparable with that of C(2), leads also to a rearrangement of the skeleton and the following pseudo-indoxyl chromophores are formed : C5m (e.g. isoreserpiline-pseudo - indoxyl) from C4a C5k (e.g. fluorocarpamine) from C4f and C5t (e.g. dihydrocorynantheine-pseudoindoxyl) from C3a. Starting with the primarily formed skeleton types, others can be derived through additional ring closures: C5c (e.g. ajmaline) bei C(7)+C(17) in C4c; C5g (e.g. rauwolfine) by C(7)+C(17)-OH in C4c; C6c (e.g. anhydro-vobasinediol) by C(17)-OH+C(3)-OH in C5a¹² ; C6a (e.g. gardneramine) by C(17)-OH+C(2)=O in C5f;

-
- 12) The skeleton type C6c can also be derived from C4c directly.

C5l (e.g. quinamine) by $C(2)+C(5)-\underline{OH}$ in C4g; C5h (e.g. pseudoakuummagine) by $C(17)-\underline{OH}+C(2)$ in C4e; C6b (e.g. corymine) by $C(17)-\underline{OH}+C(3)-\underline{OH}$ in C5g and C8a (e.g. erinine) by $C(22)-\underline{OH}+C(20)$ in C7a. The oxidative ring closures offer an explanation for the formation of the following skeleton types from C4c : C5p (e.g. eburnaphylline) by $C(17)-\underline{OH}+C(20)$; C5i (e.g. dehydro-voachalotine) by $C(17)-\underline{OH}+C(6)$, C5o (e.g. voacoline) by $C(17)-\underline{OH}+C(19)$ and C5d (e.g. picraline) by $C(5)-\underline{OH}+C(2)$ and C5u (e.g. quaternoline) by $C(22)-\underline{OH}+C(20)$ from C4e.

Finally, for the formation of some skeleton types, additional ring openings should be accepted as responsible : the cleavage of the bond $C(21)-N(b)$ yields C5r (e.g. alstonilidine) from C4a, C7a (e.g. eripine) from C6b and C5s (e.g. alstonidine) from C4a. C6d (e.g. aspidodasycarpine) results from the cleavage of $C(5)-N(b)$ in C5d, and C5y (e.g. vinoxetine) from the cleavage of $C(6)-C(7)$ in C4f: C5v (e.g. nareline) can be derived from C4e; the atoms $C(5)$, $C(6)$, $C(21)$ and $N(b)$ are involved leading to C5v.

Alternative to the formation of C3a from 2b¹ (scheme 3) is the ring closure between $N(a)$ and $C(17)$ which leads to skeleton C3b (e.g. akagerine).

A more complex reaction given in scheme 5 is necessary for explanation of alkaloid formation of type C7b (e.g. ervatamine) and C8b (e.g. ervitsine) (14, 15).

With respect to the formation of some skeleton types discussed here, there are other alternative possibilities.

The established occurrences of indole alkaloids of corynanthean-type are given in table 3. As shown, the alkaloids of this type have been detected in all three plant families. A complete summary of the occurrences is demonstrated in table 4 (for the discussion with regard to the occurrence, see part 4.3).

Scheme 5. Formation of skeleton types C7a and C8b from those of type C5a (14, 15).

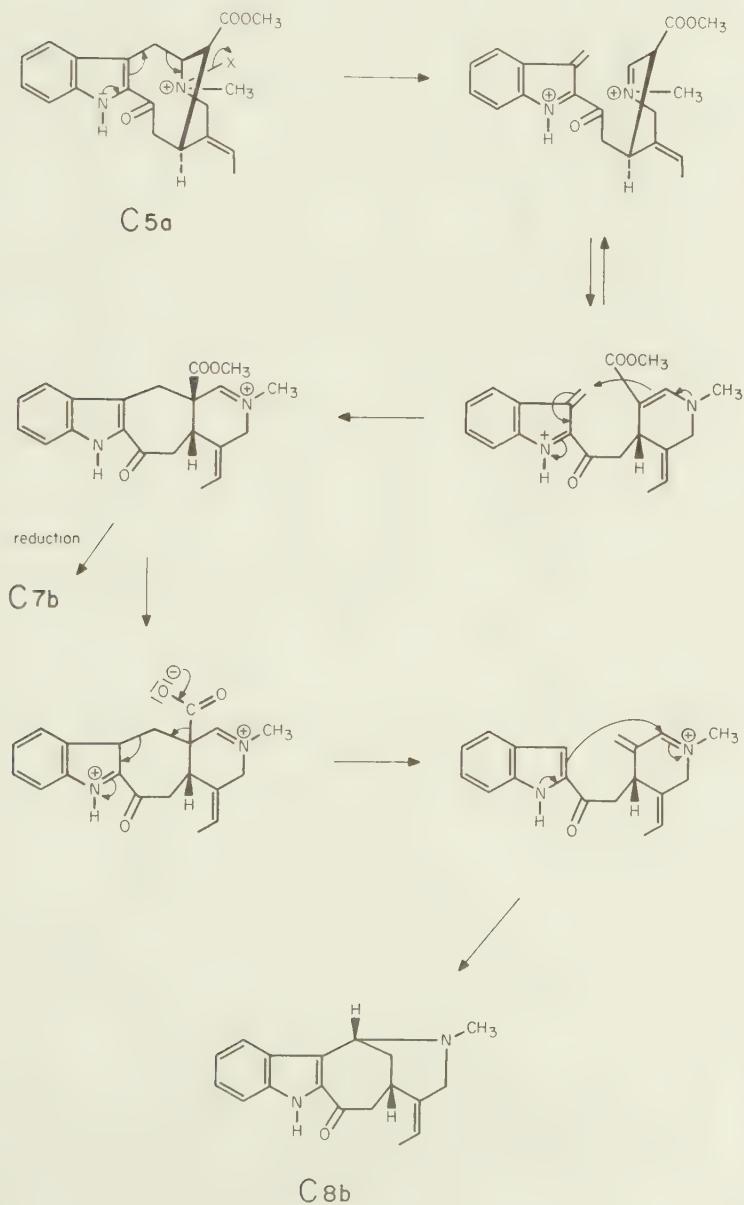


Table 3. Number of isolations of indole alkaloids of corynanthean (C) -type
skeleton types

species C3a C4a C4b C4c C4d C4e C4f C5a C5b C5c C5d C5g C5h other C-types

Plumerioideae

Plumerioideae

CARISSEAE

<i>Bonafousia</i>	4	4	1	2	2	1	3		2	3			<u>C4h:1</u> , <u>C5p:1</u> , <u>C6b:7</u> , <u>C7a:1</u> , <u>C8a:5</u>
<i>Melodinus</i>	4			1	3				1				
<i>Picralima</i>	1		2	1	1	2			2	2			<u>C5n:1</u>
<i>Pleiocarpa</i>	4	3		5			5	1					<u>C5e:1</u> , <u>C5o:1</u>

TABERNAEMONTANEAE

<i>Bonafousia</i>	1	1											
<i>Capuronetta</i>	1							4					
<i>Conopharyngia</i>	7			3		1	24	1					<u>C6c:1</u> <u>C7b:3</u>
<i>Ervatamia</i>	5			1			13						
<i>Gabunia</i>	2			1			6	2					
<i>Hazunta</i>	9		2	2			26	4					
<i>Hedranthera</i>	1						1						
<i>Muntafara</i>	1						2						
<i>Paglantha</i>	2						3						
<i>Pandaca</i>	9				1		8						<u>C7b:1</u> , <u>C8b:1</u>
<i>Peschiera</i>	7	1		6			22						<u>C6c:1</u>
<i>Stemmadenia</i>	2		1				1						
<i>Tabernaemontana</i>	2				1		7						<u>C5f:10</u> , <u>C5i:1</u> , <u>C5o:1</u>
<i>Voacanga</i>	9		1	4	7		23						

species	skeleton types												
	C3a	C4a	C4b	C4c	C4d	C4e	C4f	C5a	C5b	C5c	C5d	C5g	C5h other C-types
<i>ALSTONIAE</i>													
<i>Alstonia</i>	17	3	13	8	7	13			16	6	12	1	<u>C5e:20</u> , <u>C5r:1</u> , <u>C5s:1</u> , <u>C5u:1</u> , <u>C5v:1</u> , <u>C5d:3</u> , <u>C6e:1</u>
<i>Amsonia</i>	3	3	2	4	2	1							
<i>Aspidosperma</i>	16	24	11	16	5			2	1	3			<u>C5m:1</u> , <u>C6d:2</u>
<i>Catharanthus</i>	6	6	11	7	2	1	4	1				1	
<i>Diplorhynchus</i>	1		2	1									
<i>Geissoispermum</i>	2	2		3									
<i>Gonioma</i>	2			1		2							<u>C5k:1</u>
<i>Rhazya</i>	1	1		2	4								
<i>Tonduzia</i>	1	1	3						2				
<i>Vinea</i>	8	1	16	12	5		1	20	18	5	2	3	<u>C5y:1</u>
<i>RAUVOLFIAE</i>													
<i>Cabucala</i>	5	16	3	1	2		1	6	4		3	2	
<i>Neisosperma</i>	6	12	6	5	1		3						
<i>Ochrosia</i>	10	5	14	1				2					<u>C5m:1</u> , <u>C5n:2</u>
<i>Rauwolfia</i>	49	15	132	136	22	3	2	5	83	3			<u>C5e:2</u> , <u>C5m:1</u> , <u>C5n:1</u> , <u>C5q:1</u>
<i>Vallisia</i>	1		1	1		1							

species	Skeleton types									
	C3a	C4a	C4b	C4c	C4d	C4f	C4g	C5a	C5b	C5c C5d C5g C5h other C-types
<u>COMBACEAE</u>										
<u>GELSENIEAE</u>										
<i>Gelsemium</i>	2		2							
<i>Nostuea</i>	2		2							
<u>STRYCHNEAE</u>										
<i>Jambhina</i>	3			1						C5f:9, C5i:2, C6a:12
<i>Strychnos</i>	19	20	5	2	14	4	13			C3b:12, C5k:6
<u>RUBIAEAE</u>										
<u>CONVOLVULACEAE</u>										
<u>NAUCLEAE</u>										
<i>Adixa</i>	1	2	1	1						
<i>Sephalanthus</i>	1	2			4					
<i>Mitragyna</i>	10	18	18		63				20	
<i>Neonauclea</i>	1		1							
<i>Uncaria</i>	43	31	42	8	92				256	C5t:3
<u>CINCHONEAE</u>										
<i>Cinchona</i>	3		1				2			C5l:5
<i>Corynanthe</i>	3	3	6	7		2				
<i>Pausinystalia</i>	3	3	1	12						
<i>Rentzia</i>	1						1			
<u>MUSSANDEAE</u>										
<i>Isertia</i>	1									C5l:2
<u>GUETTARDIACEAE</u>										
<i>Guettarda</i>	1									

Table 4. Distribution of alkaloids of corynanthean(C)-type in plant families

Family	LOGANIACEAE	APOCYNACEAE	RUBIACEAE					
Subfamily		PLUMERIOIDEAE	CINCHONOIDEAE	RUBIOIDEAE	GUETTARDOIDEAE			
Tribe	GEL	STR	CAR	TAB	ALS	RAU	NAU	CIN MOS , PSY URO GUE
Number of genera	2	2	4	14	10	5	5	4 1 - - 1
Number of species	4	22	13	58	57	71	56	10 1 - - 1

Number of isolations	1801
with absolute configuration	663 = 37%
Number of structurally different alkaloids (bisindole alkaloids are counted twice)	513

2.2. Alkaloids of vincosan (D)-type

This relatively small group of alkaloids, being fairly rich on skeleton variations, apparently has two biogenetic pathways : on the one hand, rotation about the bond C(15)-C(20) in 1 (scheme 3) followed by the ring formations C(2)+C(3) and C(17)-OH+C(21) leads to D3a (e.g.vincoside), which can be accepted as the main skeleton of vincosan type, from which other skeleton types seem to be derivable (scheme 6); and on the other hand, D3a can directly be formed by condensation of tryptamine (ac) (or tryptophane (ad)) with secologanin (ae) or a direct equivalent of it.

The skeleton types D6c (e.g. peraksine) and D6b (e.g. perakine) belong probably to the former group of compounds.¹³ Reaction of D3a with NH₃ lead to D3b (e.g.lyadine). From D3a, by ring closure reactions between N(b) and C(19) D4b (e.g. cadamine), between N(a) and C(16) D4f (e.g. talbotine), between N(a) and C(19) D4g (e.g.adifoline)

- 13) Alkaloids of the type C5c (scheme 4) frequently containing a hydroxyl group on C(21), so that they are amino-hemiacetals. By such compounds, it is acceptable that an isomerisation to D6b unter participation of the double bond C(19)=C(20) can take place.

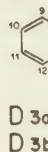
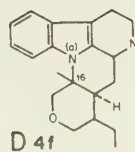
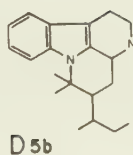
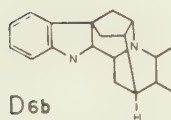
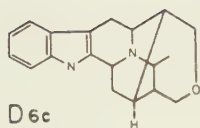
between C(14) and C(18) D4e (e.g. pauridianthinine),
 between N(b) and C(18) D4a (e.g. 3 α -dihydro-cadambine)
 and between N(a) and C(22) D4c (e.g. 10-desoxy-adifoline)
 (see scheme 6). The ammonia reaction product of D4c is
D4d (e.g. camptoneurine). The formations of D5a (e.g.
 cadambine) and D5b (e.g. deformyl-talbotinic-acid-
 methylester) from D4a and respectively D4f are obvious.
 Reductive ring cleavage of D5a can form D6a (e.g. naucleonine).
 The skeleton D5c (e.g. rubenine) is a special derivative
 of D4a in which a 5-carboxy group forms an additional ring.

.

Examples of structure and a complete list of alkaloids
 of vincosan-types are given in table 5. In table 6 the
 plant sources are given and table 7 summarizes the results.

APO

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Scheme 6.¹⁰

Distribution of alkaloids of v

Table 5. Vincosan (D)-type - examples of structure and
names of all isolated alkaloids

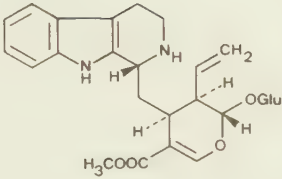
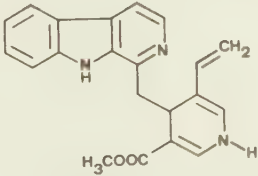
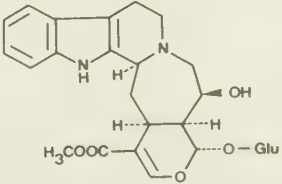
Type	Example	Alkaloids
D3a	 vincoside	cordifoline (10-desoxy-c.), dolichantoside, lyaloside, palinine, pauridianthoside, strictosidine (5α-carboxy-s.; 5-oxo-s.), vinco- side.
D3b	 lyadine	lyalidine (19-hydroxy-l.), lyadine, lyaline, pauridianthine, pauridianthanol.
D4a	 3α-dihydro-cadambine	decarbomethoxy-nauclechine, 3α- dihydro-cadambine (3β-dihydro-c.), macrolidine, naufoline.

Table 5. Cont'd

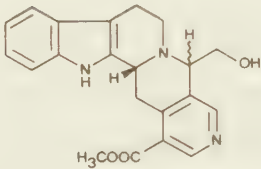
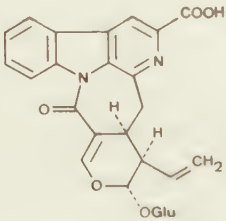
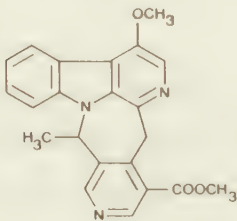
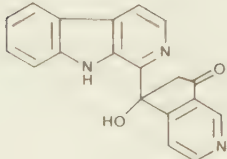
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>D4b</u>	 cadamine	cadamine (iso-c.), isodihydro-cadambine, 3 β -isodihydro-cadambine.
<u>D4c</u>	 desoxycordifoline-lactam	desoxycordifoline-lactam.
<u>D4d</u>	 camptoneurine	camptoneurine.
<u>D4e</u>		paucidanthinine.

Table 5. Cont'd

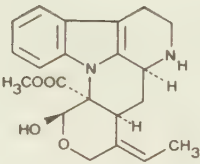
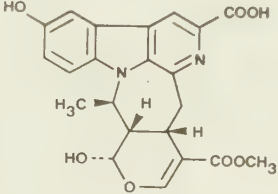
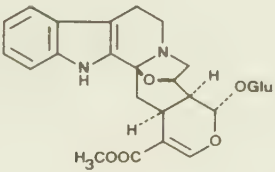
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>D4f</u>		talbotine (3,4-dehydro-t.; 3,4,5,6-tetradehydro-t.).
talbotine		
<u>D4g</u>		adifoline (10-desoxy-a.).
adifoline		
<u>D5a</u>		cadambine.
cadambine		

Table 5. Cont'd

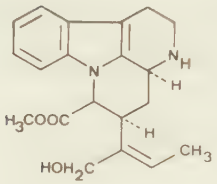
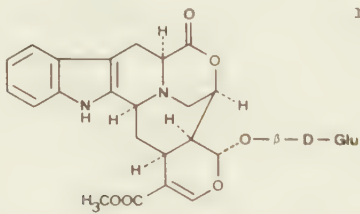
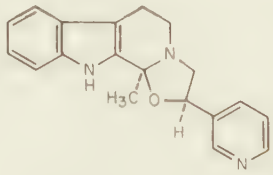
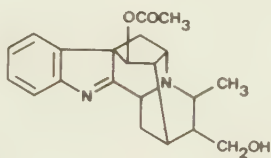
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>D5b</u>		deformyl-talbotinic acid methyl- ester.
	deformyl-talbotinic acid methylester	
<u>D5c</u>		rubenine.
	rubenine	
<u>D6a</u>		α -naucleonidine, β -naucleonidine, α -naucleonine, β -naucleonine.
	α -naucleonine	

Table 5. Cont'd

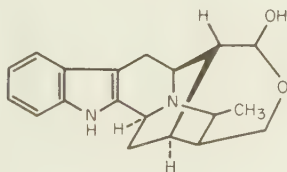
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>D6b</u>		perakine, raucaffrinoline.



perakine

D6c

macrosalhinine, peraksine.



peraksine

Again alkaloids of vincosan(D)-type occur in all three plant families.

Table 6. Number of isolations of indole alkaloids of vincosan(D)-type

[illegible]

Table 7. Distribution of alkaloids of vincosan(D)-type in plant families

Family	LOGANIACEAE			APOCYNACEAE			RUBIACEAE					
Subfamily				PLUMERIOIDEAE			CINCHONOIDEAE			RUBIOIDEAE GUETTARDOIDEAE		
Tribe	GEL	STR	CAR	TAB	ALS	RAU	NAU	CIN	MUS	PSY	URO	GUE
Number of genera	-	1	1	1	3	1	4	-	-	1	1	-
Number of species	-	2	1	1	3	6	5	-	-	1	2	

Number of isolations	58
with absolute configuration	17 = 30%
Number of structurally different alkaloids	44

2.3. Alkaloids of vallesiachotaman(V)-type

As results from scheme 2, the bases of vallesiachotaman-type can also be derived from 2b, the common preliminary step for corynanthean- and vincosan-groups. The cyclisation between C(17)-OH and N(b) in 2b leads to V3 (e.g. antirrhine), which can be transformed to V4 (e.g. angustine) by ring closure [C(22)-OH or C(17) + C(21)], scheme 7. Hitherto, only these two skeleton types could be detected, although distributed in three plant families, tables 8, 9, 10.

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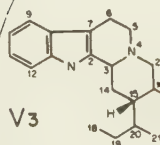




Table 8. Vallesiachotaman (V)-type - examples of
structures and names of all isolated alkaloids

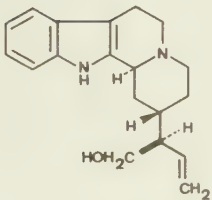
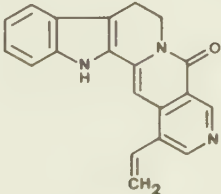
<u>Type</u>	<u>Example</u>	<u>Alkaloid</u>
V3	 antirhine	antirhine (α.-methochloride; 18,19-dihydro-α.-β-methochloride), hunterburnine-α-methochloride, hunterburnine-β-methochloride, vallesiachotamine.
V4	 angustine	angustidine, angustine, angustoline, glucoalkaloid, 10-β-D-glucosyloxy-vincoside-lactam, nauclefine, nauclefine, parvine, rubescine, strictosamide, strictosidine-lactam, 3α,5α-tetrahydro-desoxy-cordifoline-lactam, 3β,5α-tetrahydro-desoxy-cordifoline-lactam.

Table 9. Number of isolations of indole alkaloids
of vallesiachotaman(V)-type

	species	Skeleton types	
		V3	V4
<u>APOCYNACEAE</u>			
<u>Plumerioideae</u>			
<u>CARISSEAE</u>			
<i>Hunteria</i>	2	5	
<i>Pleiocarpa</i>	1	2	
<u>ALSTONIEAE</u>			
<i>Amsonia</i>	2	2	1
<i>Catharanthus</i>	1	1	
<i>Rhazya</i>	1	1	1
<u>RAUVOLFIEAE</u>			
<i>Ochrosia</i>	1	1	
<i>Vallesia</i>	1	1	
<u>STRYCHNACEAE</u>			
<u>STRYCHNEAE</u>			
<i>Strychnos</i>	20	2	47
<u>RUBIACEAE</u>			
<u>Cinchonoideae</u>			
<u>NAUCLEEAE</u>			
<i>Adina</i>	1		4
<i>Mitragyna</i>	2		2
<i>Nauclea</i>	1		1
<i>Sarcocephalus</i>	2		7
<i>Uncaria</i>	3		8
<u>Guettardoideae</u>			
<u>GUETTARDEAE</u>			
<i>Antirhea</i>	1	1	

Table 10. Distribution of alkaloids of vallesiachotaman(V)-type in plant families

Family	LOGANIACEAE		APOCYNACEAE		RUBIACEAE							
Subfamily			PLUMERIOIDEAE		CINCHONOIDEAE		RUBIOIDEAE		GUETTARDOIDEAE			
Tribe	GEL	STR	CAR	TAB	ALS	RAU	NAU	CIN	MUS	PSY	URO	GUE
Number of genera	-	1	2	-	3	2	5	-	-	-	-	1
Number of species	-	20	3	-	4	2	9	-	-	-	-	1

Number of isolations	87
with absolute configuration	77 = 89%
Number of structurally different alkaloids	19

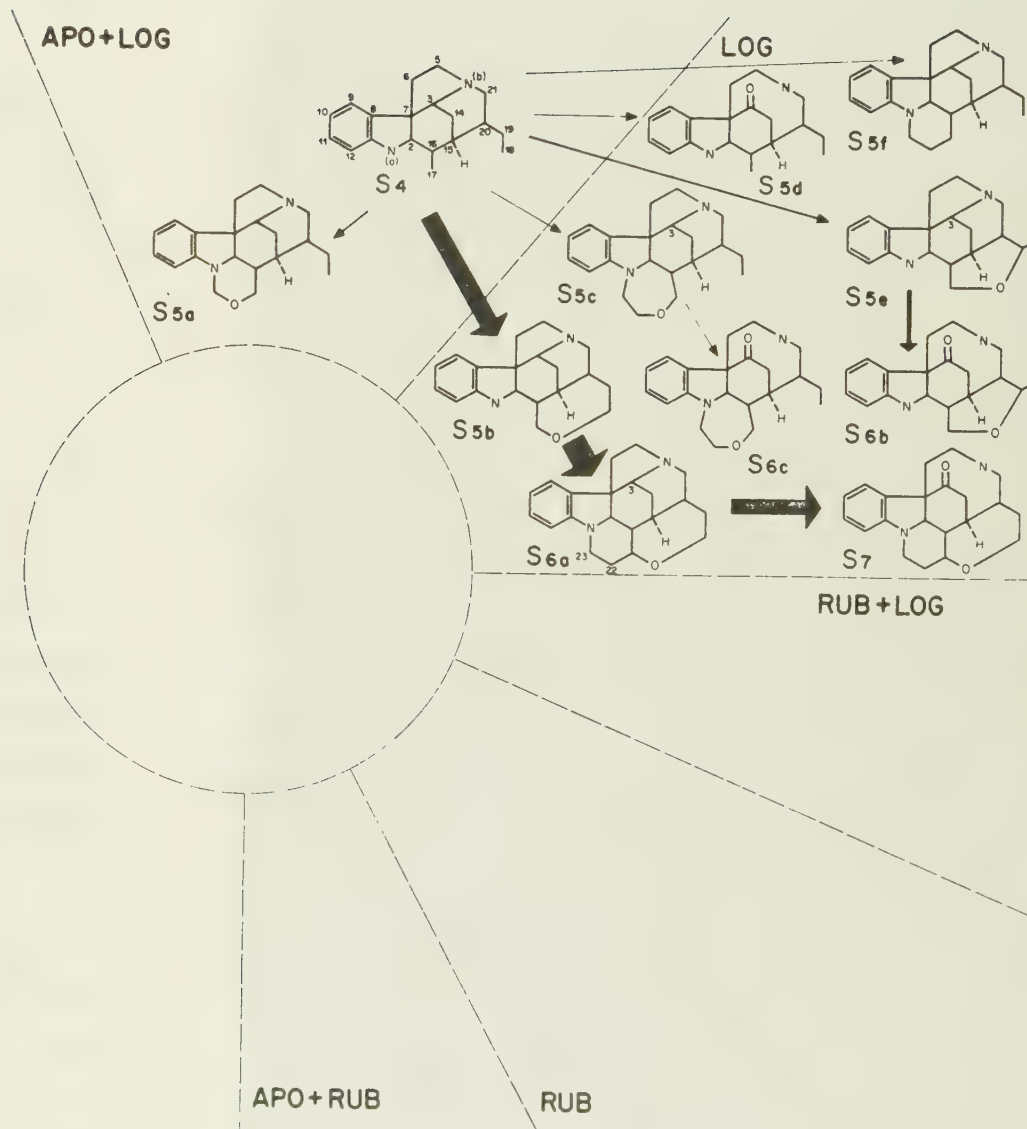
2.4. Alkaloids of strychnan (S)-type

This group of alkaloids, being one of the most populated class of indole alkaloids, is distributed on 11 skeleton types given in scheme 8. The S- and A-types have a common preliminary step : A3 (scheme 2). From the simplest skeleton type S4 (e.g. akuammicine), ring closures between C(17)-OH and C(19) leads to S5e (e.g. spermostrychnine) and between C(17)-OH and C(18) to S5b (e.g. diaboline), compare table 11. By built-in of an additional C₂-unit on N(a), followed by a C,C-linkage with C(17), S5f (e.g. isostrychnine) is obtained from S4, and S6a (e.g. strychnine) from S5b. An ether linkage between C(17) and the C₂-unit on N(a) (e.g. acetate) forms S5c (e.g. tsilanine). Instead of a C₂-unit, a C₁-unit can also be built in on N(a), giving rise to S5a (e.g. geissospermine) from S4. In this case however, it should be emphasized that C₁-unit in question does not originate from formaldehyde but rather comes from HC(17)=O group of another "monomeric" indole alkaloid. Fairly simple oxidizibility at C(3), leading to the cleavage of the bond C(3)-N(b), is a remarkable characteristic of S-type : S6a → S7 (e.g. icajine), S5c → S6c (e.g. rindline), S4 → S5d (e.g. strychnosilidine), and S5e → S6b (e.g. strychnobrasiline). A complete list of alkaloids of strychnan type with corresponding examples of structures is given in table 11.

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Scheme 8.¹⁰ Distribution of alkaloids of strychnan (S)-type in plant families.

Table 11. Strychnan (S)-type - examples of structures
and names of all isolated alkaloids

(° = bisindole alkaloid, given twice if necessary)

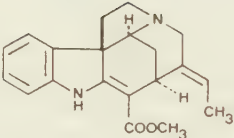
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>S4</u>	 akuammicine	N-acetyl-2,16-dihydro-2β,16α-akuammicinal, afrocurarine°, akuammicine (a.-methochloride; a.-N-oxide; 19,20-dihydro-a.; 2,16-dihydro-akuammicine; 18- or 19-hydroxy-19,20-dihydro-a.; 11-methoxy-a.; N_(a)-methyl-2,16-dihydro-a.; pre-a.; pseudo-a.), C-alkaloid-A° (a.-D°; bisnor-a.-D°; a.-E°; a.-F°; a.-G°; a.-H°; bisnor-a.-H°), alstovine, angustimycine, C-calebassine°, compactinervine, C-curarine I° (bisnor-C-c.°), 18-desoxy-Wieland-Gumlich aldehyde; C-dihydro-toxiferine° (bisnor-d.°; bisnor-d.-di-N-oxide°; bisnor-d.-N-oxide°; nor-d.°), echitamidine, C-fluorocurarine (nor-f.), geissoschizoline, lochneridine (20-epi-l.), mossamine, retuline (N_(a)-desacetyl-17-O-acetyl-18-hydroxy-iso-r.; N_(a)-desacetyl-18-hydroxy-i.; N_(a)-desacetyl-iso-r.; desacetyl-r.; 18-hydroxy-iso-r.; iso-r.; r.-N-oxide), sewarine, strychnobiline° (12'-hydroxy-iso-s.°; iso-s.°), C-toxiferine I°, tsilanimbine, tubifolidine, tubifoline, vincanicine, vincanidine, vinervine, vinervinine.

Table 11. Cont'd

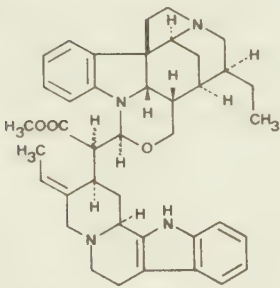
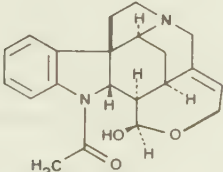
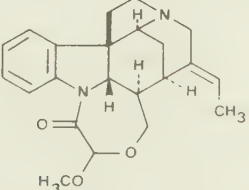
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>S5a</u>	 geissospermine	geissospermine°, geissosolosi- mine°, strychnobiline° (12'- hydroxy-iso-s.; iso-s.).
<u>S5b</u>	 diaboline	caracurine II° (c.-II-metho- salt°), caracurine V° (c.-V-N- oxide°; C-V-di-N-oxide°), diabo- line (O-acetyl-d.; 2,16-dehydro- d.; 11-methoxy-2,16-dehydro-d.; 11-methoxy-d.), henningsoline (O-acetyl-h.), jobertine, 11- methoxy-henningsamine, Wieland-Gumlich aldehyde (N_(b)-W.- chlormethylate).
<u>S5c</u>	 tsilanine	tsilanine (O-demethyl-t.; 10- methoxy-O-demethyl-t.; 10- methoxy-t.).

Table 11. Cont'd

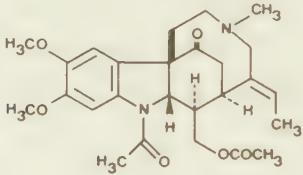
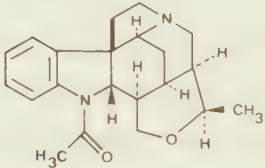
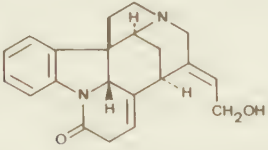
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>S5d</u>	 strychnosilidine	strychnosilidine, strychnosiline, tabascanine.
<u>S5e</u>	 spermostrychnine	spermostrychnine (12-hydroxy-11-methoxy-s.), splendoline (iso-s.), strychnosplendine (N-acetyl-iso-s.; N _(a) -acetyl-s.; 12-hydroxy-11-methoxy-N _(a) -acetyl-s.; iso-s.), strychnospermine (desacetyl-s.).
<u>S5f</u>	 isostrychnine	isostrychnine.

Table 11. Cont'd

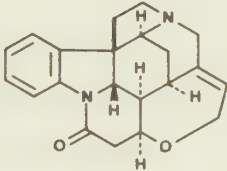
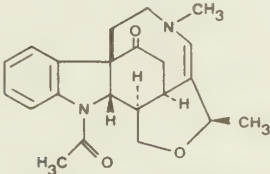
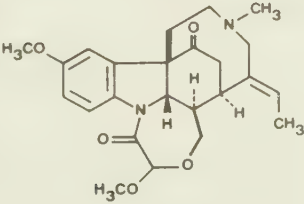
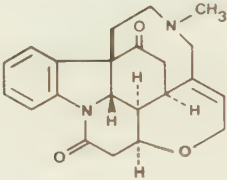
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>S6a</u>	 strychnine	brucine (b.-N-oxide; pseudo-b.), α -colubrine, β -colubrine, strychnine (12-hydroxy-11-methoxy-s.; 12-hydroxy-s.; 15-hydroxy-s.; 3-methoxy-s.; pseudo-s.; s.-N-oxide).
<u>S6b</u>	 strychnobrasiline	N _(a) -acetyl-O-methyl-strychnosplendine, isosplendine, strychnobrasiline (10,11-dimethoxy-s.; 12-hydroxy-11-methoxy-s.; 10-methoxy-s.), strychnofendlerine (12-hydroxy-11-methoxy-s.).
<u>S6c</u>	 rindline	holstiine, holstiline, rindline.

Table 11. Cont'd

<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>S7</u>	 icajine	N-cyano-sec-pseudobrucine, N-cyano-sec-pseudostrychnine, 12-hydroxy-11-methoxy-pseudostrychnine, icajine (15-hydroxy-i.; i.-N-oxide), N-methyl-sec-pseudobrucine, N-methyl-sec-pseudostrychnine (19,20-α-epoxy-11,12-dimethoxy-N-m.; 19,20-α-epoxy-10,11-dimethoxy-N-m.; 19,20-α-epoxy-15-hydroxy-N-m; 19,20-α-epoxy-15-hydroxy-12-methoxy-N-m.; 19,20-α-epoxy-12-methoxy-N-m.; 12-hydroxy-N-m.; 10- or 11-methoxy-N-m.), novacine (19,20-α-epoxy-n.; 15-hydroxy-n.), pseudo-α-colubrine, pseudo-β-colubrine (19,20-α-epoxy-N-methyl-sec-p.; N-methyl-sec-p.), N-cyano-sec-pseudo-colubrine, vomicine (19,20-α-epoxy-15-hydroxy-v.; 19,20-α-epoxy-11-methoxy-v.; 19,20-α-epoxy-v.).

It is a very remarkable fact that alkaloids of strychnan(S)-type, so far, have not been detected in the plant family of Rubiaceae. Besides the very special type S5a only alkaloids of skeleton type S4 are produced from Apocynaceae, see tables 12 and 13.

Table 12. Number of isolations of indole alkaloids of
strychnan(S)-type

	species	Skeleton types										
		S4	S5a	S5b	S5c	S5d	S5e	S5f	S6a	S6b	S6c	S7
<u>POCYNACEAE</u>												
<u>Lumerioideae</u>												
<u>VARISSEAE</u>												
<i>Lunteria</i>	2		2									
<i>Pieralima</i>	1		2									
<i>Pleiocarpa</i>	1		3									
<u>TABERNAEMONTANEAE</u>												
<i>Ervatamia</i>	1		1									
<i>Mazunta</i>	2		2									
<i>Pandaca</i>	1		1									
<u>ALSTONIEAE</u>												
<i>Alstonia</i>	5		12									
<i>Amsonia</i>	2		2									
<i>Aspidosperma</i>	1		1									
<i>Catharanthus</i>	3		7									
<i>Diplorrhynchus</i>	1		2									
<i>Geissospermum</i>	2		1	3								
<i>Rhazya</i>	1		2									
<i>Vinca</i>	3		9									
<u>RAUVOLFIEAE</u>												
<i>Cabucala</i>	1		1									
<u>LOGANIACEAE</u>												
<u>STRYCHNEAE</u>												
<i>Strychnos</i>	49	136	3	65	4	4	14	1	55	7	3	64

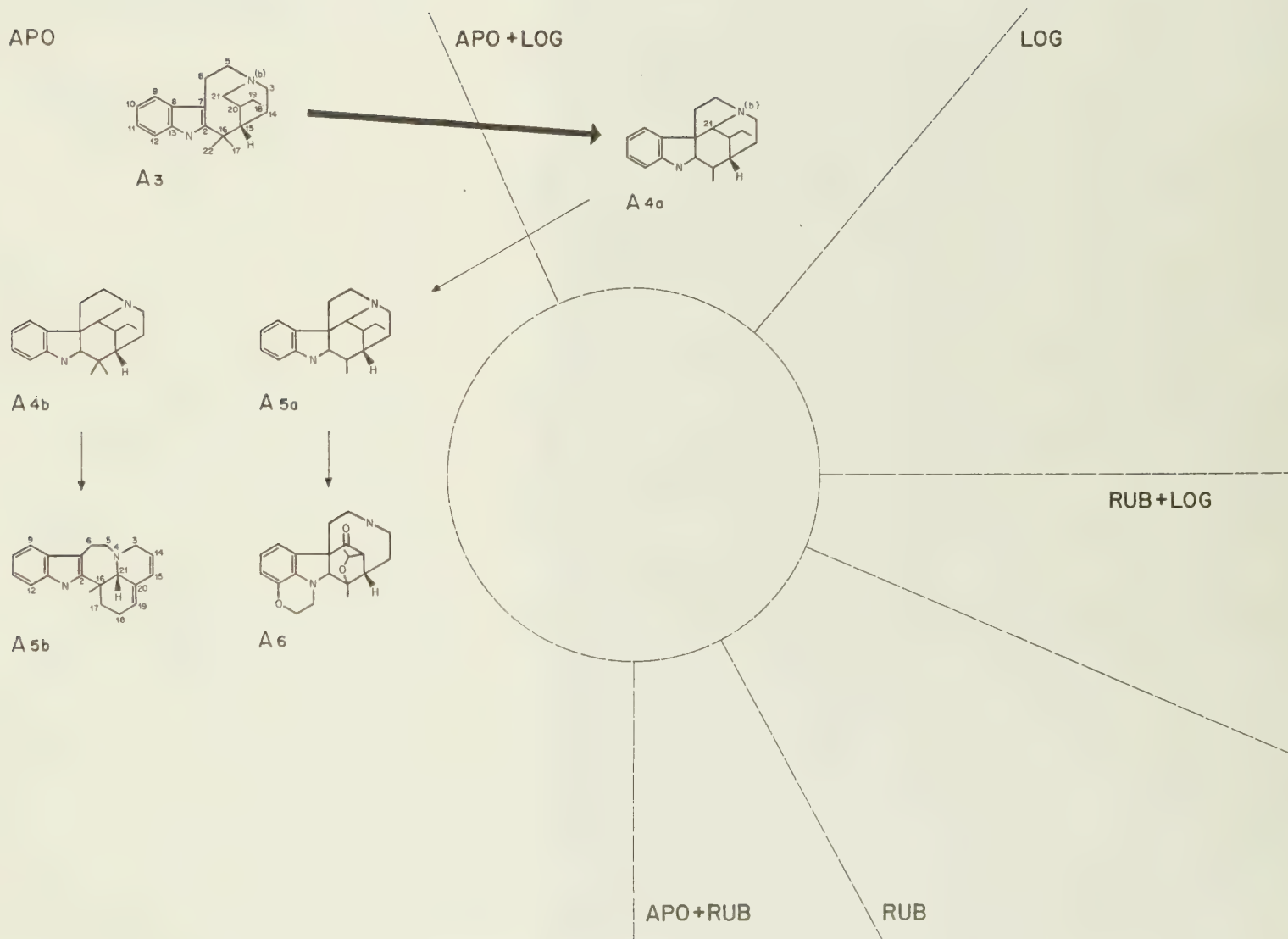
Table 13. Distribution of alkaloids of strychnan(S)-type in plant families

Family	LOGANIACEAE	APOCYNACEAE	RUBIACEAE									
Subfamily		PLUMERIOIDEAE	CINCHONOIDEAE RUBIOIDEAE GUETTARDOIDEAE									
Tribe	GEL	STR	CAR	TAB	ALS	RAU	NAU	CIN	MUS	PSY	URO	GUE
Number of genera	-	1	3	3	8	1						
Number of species	-	49	4	4	18	1						

Number of isolations	407
with absolute configuration	139 = 34%
Number of structurally different alkaloids (bisindole alkaloids are counted twice)	150

2.5. Alkaloids of aspidospermatan(A)-type

This group of natural compounds is distributed among six types of skeletons (scheme 9). Starting with the common preliminary step of the aspidospermatan- and strychnan-types, A3 (e.g. stemmadenine) the cyclisations between C(7) and C(21) yields A4b (e.g. precondylocarpine), and the decarboxylation leads to the main group of this type of alkaloids A4a (e.g. tubotaiwine). Oxidation of A4a at C(21) followed by the cleavage of the bond C(21)-N(b) produces A5a (e.g. geissovelline) from which by two successive cyclisations under incorporation of an external C₂-unit, A6a (e.g. dichotine) is obtained. The skeleton type A5b (e.g. andranginine), of which only two alkaloid isolations are known, can be derived from A4b represented mainly by precondylocarpine (17). In contrast to the other skeleton types of the aspidospermatan group andranginine is a racemate which favours a achiral intermediate between A4b and A5b (17). The examples for skeleton types of the aspidospermatan group and the names of all isolated alkaloids are given in table 14. The plants from which the alkaloids were isolated are listed in table 15, which is summarized in table 16.



Scheme 9.¹⁰ Distribution of alkaloids of aspidospermatan (A)-type in plant families.

Table 14. Aspidospermatan (A)-type - examples of
structure and names of all isolated alkaloids

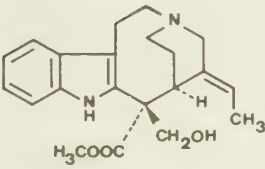
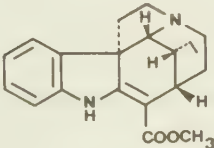
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>A3</u>	 stemmadenine	stemmadenine (deformo-s.).
<u>A4a</u>	 tubotaiwine	aspidospermatidine, (N _(a) -acetyl-a.; 11,12-dihydroxy-N-acetyl-a.; N _(a) - methyl-a.), aspidospermatine (N- acetyl-11-hydroxy-a.; desacetyl-a.; 19,20-dihydro-a.), condylocarpine (19,20-dihydro-c.; 11-methoxy-19,20- dihydro-c.), limatine (11-methoxy-l.), limatinine (11-methoxy-l.), tubotaiwine (t.-N-oxide).

Table 14. Cont'd

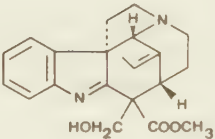
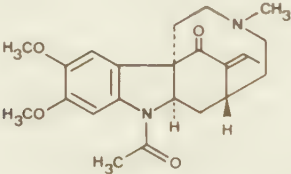
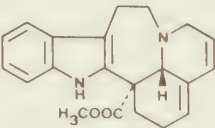
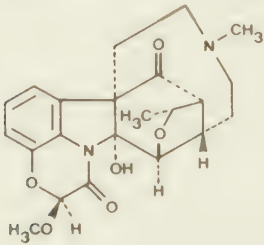
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>A4b</u>	 precondylocarpine	precondylocarpine.
<u>A5a</u>	 geissovelline	geissovelline.
<u>A5b</u>	 andranginine	andranginine.
<u>A6</u>	 dichotine	dichotine (11-methoxy-d.).

Table 15. Numbers of isolations of indole alkaloids of
aspidospermatan (A)-type

		Skeleton types					
	species	<u>A3</u>	<u>A4a</u>	<u>A4b</u>	<u>A5a</u>	<u>A5b</u>	<u>A6</u>
<u>APOCYNACEAE</u>							
<u>Plumerioideae</u>							
<i>CARISSEAE</i>							
<i>Melodinus</i>	2	1	3				
<i>Pleiocarpa</i>	1		1				
<i>TABERNAEMONTANEAE</i>							
<i>Conopharyngia</i>	1		2				
<i>Hazunta</i>	1	1					
<i>Pandaca</i>	4	1	5				
<i>Stemmadenia</i>	3	3					
<i>Tabernaemontana</i>	1		1				
<i>ALSTONIEAE</i>							
<i>Alstonia</i>	2		2				
<i>Amsonia</i>	1		1				
<i>Aspidosperma</i>	9	1	18			2	
<i>Catharanthus</i>	1	1					
<i>Craspidospermum</i>	2	2	2			2	
<i>Diplorrhynchus</i>	1	1	1				
<i>Geissospermum</i>	1				1		
<i>RAUVOLFIEAE</i>							
<i>Vallesia</i>	1		3	1			2
<u>LOGANIACEAE</u>							
<i>STRYCHNEAE</i>							
<i>Strychnos</i>	1		1				

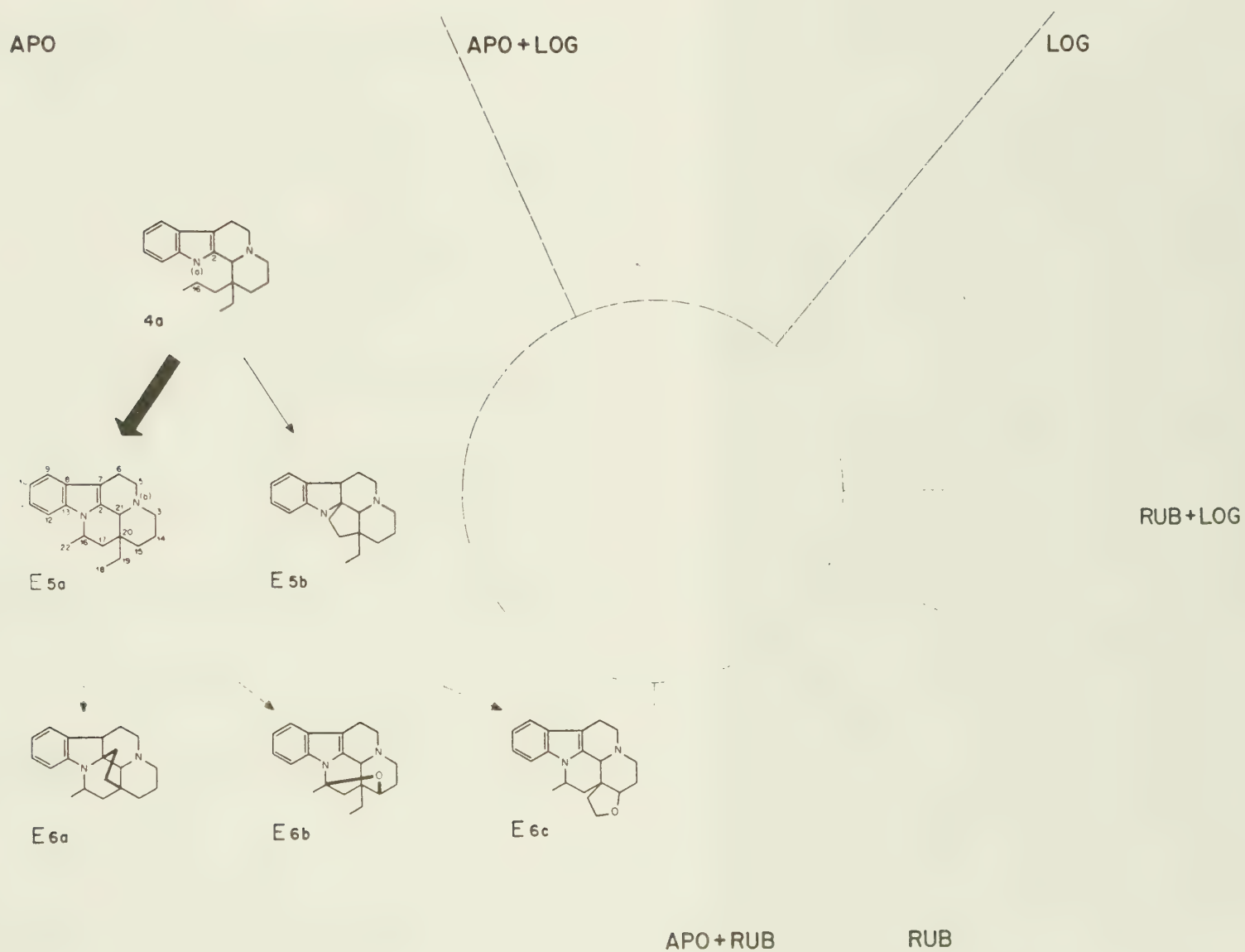
Table 16. Distribution of alkaloids of aspidospermatan(A)-type in plant families

Family	LOGANIACEAE			APOCYNACEAE			RUBIACEAE						
Subfamily				PLUMERIOIDEAE			CINCHONOIDEAE			RUBIOIDEAE		GUETTARDOIDEAE	
Tribe	GEL	STR		CAR	TAB	ALS	RAU	NAU	CIN	MUS	PSY	URO	GUE
Number of genera	1			2	5	7	1						
Number of species	1			3	10	17	1						

Number of isolations	59
with absolute configuration	39 = 65%
Number of structurally different alkaloids	24

2.6. Alkaloids of eburnan (E)-type.

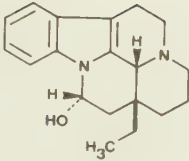
This and both of the following alkaloid types being derived from the common preliminary steps 2a and 3a (scheme 2) have a rearranged secologanin skeleton. Till now, five variations of skeleton are known composing the eburnan group, scheme 10. Cyclisation between C(16) and N(a) in precursor 4a (derived from 3a by ring closure) forms E5a (e.g. eburnamine). On the other hand, another cyclisation between C(16) and C(2) in the same precursor yields E5b (e.g. andrangine). Starting with E5a, ring closure between C(2) and C(18) leads to E6a (e.g. schizogamine); ether linkage between C(15) and C(16) to E6b (e.g. craspidospermine), and formation of the bond between C(15) and C(18)-OH to E6c (e.g. cuanzine). For structural examples and corresponding alkaloids, see table 17. The isolation can be depicted from table 18 and 19.



Scheme 10.¹⁰ Distribution of alkaloids of Eburnan (E)-type in plant families.

Table 17. Eburnan (E)-type - examples of structure and names of all isolated alkaloids

(° = bisindole alkaloid, given twice if necessary)

<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>E5a</u>	 eburnamine	eburnamenine, eburnamine (14,15-dehydro-e.; iso-e.; O-methyl-e.), eburnamonine (11-methoxy-e.), paucivenine°, pleiomutine°, umbellamine°, vincamine (apo-14,15-dehydro-v.; apo-v.; 14,15-dehydro-v.; 16-epi-14,15-dehydro-v.; 16-epi-v.; 12-methoxy-14,15-dehydro-v.), vincaminine, vincine (14,15-dehydro-epi-v.; 14,15-dehydro-v.; 16-epi-14,15-dehydro-v.), vincinine.

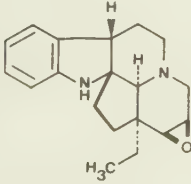
<u>E5b</u>	 andrangine	andrangine, criophylline°, schizophylline, vallesamidine.
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Table 17. Cont'd

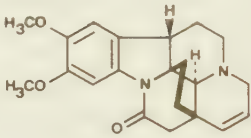
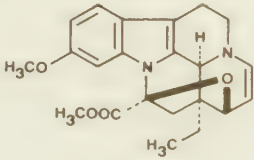
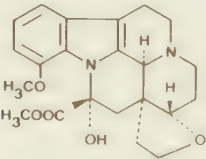
Type	Example	Alkaloids
<u>E6a</u>	 schizogamine	schizogaline (iso-s.), schizogamine (iso-s.), schizozygine, α-schizozygol.
<u>E6b</u>	 craspidospermine	craspidospermine, criocerine, vincarodine.
<u>E6c</u>	 cuanzine	cuanzine, decarbomethoxy-apo-cuanzine.

Table 18. Number of isolations of indole alkaloids of
eburnan (E) -type

		Skeleton types				
	species	<u>E5a</u>	<u>E5b</u>	<u>E6a</u>	<u>E6b</u>	<u>E6c</u>
<u>APOCYNACEAE</u>						
<u>Plumerioideae</u>						
<u>CARISSEAE</u>						
<i>Hunteria</i>	3	7				
<i>Melodinus</i>	3	4				
<i>Pleiocarpa</i>	3	6				
<u>TABERNAEMONTANEAE</u>						
<i>Anacampta</i>	1	7				
<i>Crioceras</i>	2	6	2		1	
<i>Pandaca</i>	1	1				
<i>Schizosygia</i>	1		1	6		
<i>Voacanga</i>	1	1				2
<u>ALSTONIEAE</u>						
<i>Amsonia</i>	3	7				
<i>Aspidosperma</i>	3	4				
<i>Catharanthus</i>	1				1	
<i>Craspidospermum</i>	2	2	1		1	
<i>Gonioma</i>	1	1				
<i>Haplophyton</i>	1	3				
<i>Rhazya</i>	1	3				
<i>Vinca</i>	4	18				
<u>RAUVOLFIEAE</u>						
<i>Vallesia</i>	1		1			

Table 19. Distribution of alkaloids of eburnan(E)-type in plant families

Family	LOGANIACEAE	APOCYNACEAE	RUBIACEAE				
Subfamily		PLUMERIOIDEAE	CINCHONOIDEAE	RUBIOIDEAE	GUETTARDOIDEAE		
Tribe	GEL STR	CAR TAB ALS RAU	NAU CTN MUS	PSY URO	GUE		
Number of genera		3 5 8 1					
Number of species		9 6 16 1					

Number of isolations	86
with absolute configuration	40 = 47%
Number of structurally different alkaloids	42

2.7. Alkaloids of plumeran(P)-type

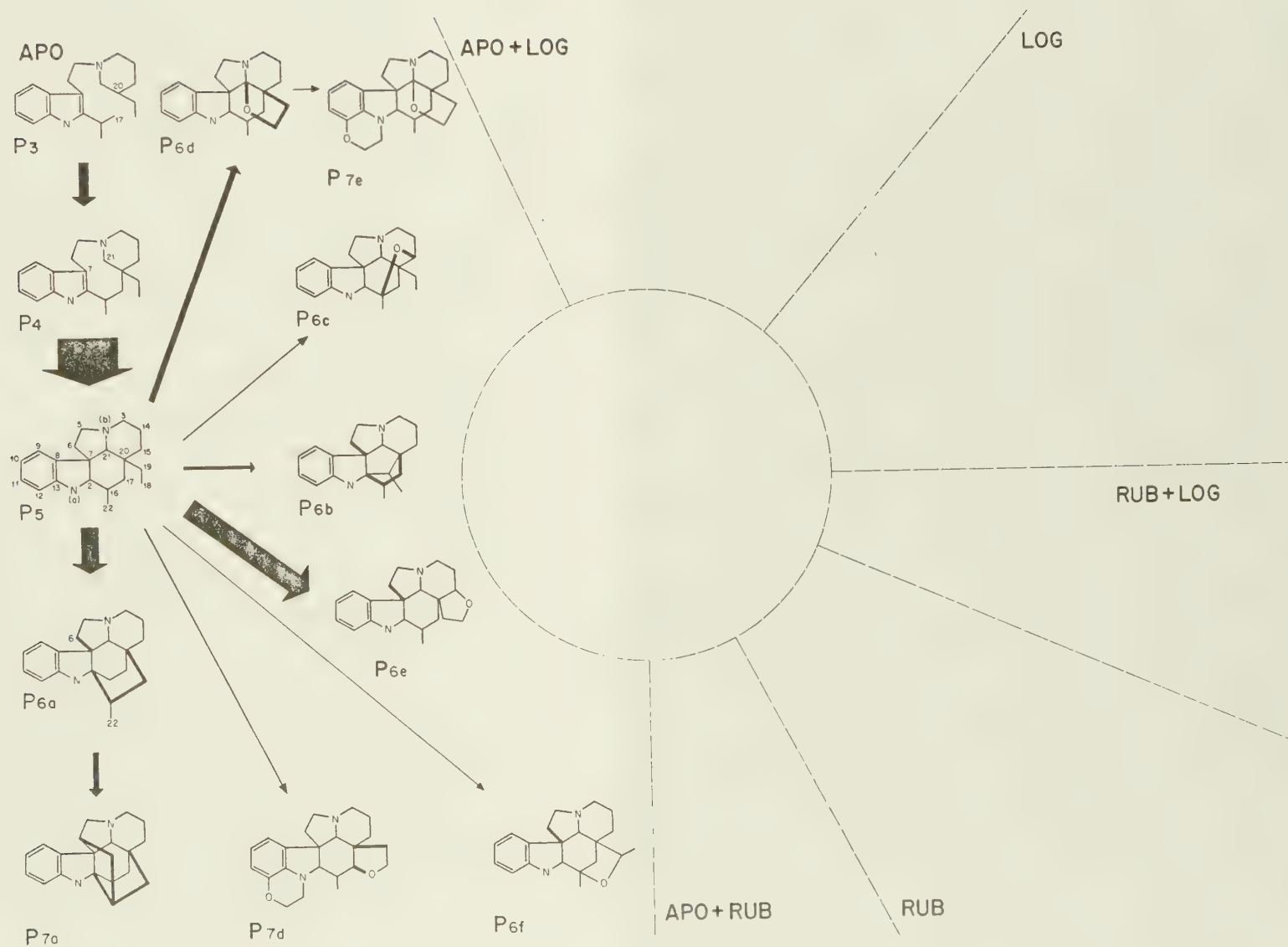
This second largest group of indole alkaloids has already been the subject of a detailed chemotaxonomic study (2). We considered the further results of investigations undertaken since then.

Starting with P4 (e.g. quebrachamine) (scheme 11) the skeletons of ibogan(J)-type (see later) can be derived over P3 (e.g. tetrahydro-secodine) obtained by the cleavage of the ring between C(17) and C(20) in P4, on the one hand, and on the other hand, various ring closure reactions form the main skeleton types of plumeran group.

Formation of a new bond between C(7) and C(21) in P4 leads to P5 (e.g. tabersonine). Various cyclisations in P5 provide the following variations : $[C(2) + C(18)] \rightarrow \underline{P6a}$ (e.g. venalstonine); $[C(2) + C(19)] \rightarrow \underline{P6b}$ (e.g. vindolinine); $[C(15)-OH + C(16)] \rightarrow \underline{P6c}$ (e.g. cathovaline); $[C(18) + C(21)] \rightarrow \underline{P6d}$ (e.g. haplophytine); $[C(16) + C(19)-OH] \rightarrow \underline{P6f}$ (e.g. melobaline) and $[C(15)-OH + C(18)] \rightarrow \underline{P6e}$ (e.g. beninine). Furthermore, from P5, P7d (e.g. neblinine) can be derived by cyclisation between C(17) and C(18)-OH followed by an additional ring closure including an external C_2 -unit (e.g. acetate) between N(a) and C(12)-OH. A similar variation of P6d is P7e (e.g. alalakine). P7a (e.g. kopsanole) can be obtained by the

formation of a new ring between C(6) and C(22) in P6a, scheme 11. From a specific rearrangement of P7a derive P7b (e.g. decarbomethoxy-isokopsine) and P7c (e.g. fruticosine).

The absolute configuration demonstrated for P6- and P7 types in scheme 11 corresponds to that of the natural bases of this group isolated so far. The names of the plumeran alkaloids with the corresponding structure examples are given in table 20. The exclusive occurrence of these alkaloids in the subfamily Plumerioideae of Apocynaceae provides a reason for the naming of this group and is explicitly given in table 21 and 22.



Scheme 11.¹⁰ Distribution of alkaloids of plumeran (P)-type in plant families.

Table 20. Plumeran (P)-type - examples of structureand names of all isolated alkaloids

(° = bisindole alkaloid, given twice if necessary)

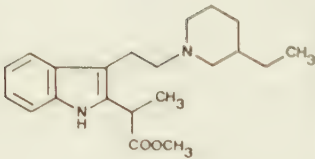
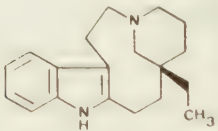
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>P3</u>	 tetrahydro-secodine	decarbomethoxy-tetrahydro-secodine (16,17-dihydro-s.; 16,17-dihydro-s.-17-ole), presecamine° (dihydro-p.°; 15,20,15',20'-tetrahydro-p.°), secamine° (decarbomethoxy-tetrahydro-s.°; dihydro-s.°; 15,20,15'20'-tetrahydro-s.°), tetrahydro-secodine (tetrahydro-s.-17-ole).
<u>P4</u>	 quebrachamine	conoflorine (c.-diole; c.-7-hydroxy indolenine; 12-methoxy-c.), ervinidine, quebrachamine (12-methoxy-qu.; N-methyl-qu.), rhazidigenine (r.-N-oxide), vincadine (14,15-dehydro-epi-v.; 14,15-dehydro-v.; epi-v.), vincaminoreine, vincaminoridine, vincaminorine.

Table 20. Cont'd

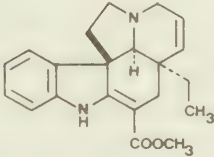
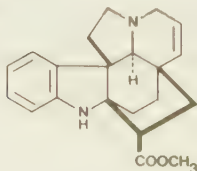
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
P5	 tabersonine	N-acetyl-N-depropionyl-aspido- albinole, aspidocarpine (O-de- methyl-a.), aspidodispermine (de- soxy-a.), aspidolimidinol, aspido- limine, aspidospermidine (N-acetyl- a.; 16-carbomethoxy-16-hydroxy- 14,15-epoxy-3-oxo-1,2-dehydro-a.; 1,2-dehydro-a.; 20,21-epi-a.; 20,21-epi-a.-N-oxide; N-formyl-a.; N_(a)-methyl-a.), aspidospermine (demethoxy-a.; demethyl-a.; des- acetyl-a.; N-methyl-desacetyl-a.), baloxine, catharine°, catha- rinine°, cathaphylline, catharosine, cathovalinine, criophylline°, cylindrocarine (N-benzoyl-c.; 12-demethoxy-N-acetyl-c.; N-formyl- c.; 19-hydroxy-N-acetyl-c.; 19-hydroxy-N-benzoyl-c.; 19-hydroxy- N-cinnamoyl-c.; 19-hydroxy-c.; 19-hydroxy-N-dihydrocinnamoyl-c.; 19-hydroxy-N-formyl-c.; methyl-c.), cylindrocarpidine (homo-c.; 5-oxo-c.), cylindrocarpine (N-acetyl-c.-ole; N-formyl-c.-ole), 11-de- methyl-aspidolimidine, dimer III°, eburcine, eburine, eburine, echitoserpidine, echitoserpine, echitovenaldine, echitovenidine, echitovenine, ervafolidine° (iso-e.°), ervafoline°, ervamine, ervincinine, ervinidinine, fendlispermine, folicangine°, hazun- tine, hazuntinine, hoerhammericine, hoerhammerinine, leuro-

Table 20. Cont'd

<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>P5</u> cont'd		
		colombine°, leurocristine°, leurosidine°, leurosine° (iso-l.°), limapodine (11-methoxy-l.), limaspermine (11-methoxy-l.), lochnericine, lochnerinine, meloceline, melocelinine, minovincine (11-methoxy-m.; 3-oxo-m.; 5-oxo-m.), minovincinine (14,15-dehydro-19- epi-m.; 19-epi-m.; 11-methoxy-m.), minovine, palosine (de- methoxy-p.; O-demethyl-p.), paucivenine°, pleurosine°, pseudo- vincaleukoblastine-diol°, pycnanthinine°, pyrifolidine (1,2- dehydro-desacetyl-p.; desacetyl-p.), scandomeline (epi-s.), scandomelonine (epi-s.), spegazzinidine, spegazzinine, tabernamine°, tabersonine (19-epi-19-hydroxy-t.; 11-hydroxy-t.; 19-hydroxy-t.; 19R-hydroxy-t.; 19S-hydroxy-t.; 11-methoxy-t.; 3-oxo-t.; t.-N _(b) -oxide), vallesine, vinblastine° (desacetoxo-v.°), vincadifformine (14,15-epoxy-3-oxo-v.; 11-methoxy-v.), vinca- thicine°, vincovalicine°, vincovaline°, vincovalinine°, vindoline (demethoxy-v.; desacetyl-v.), vindorosine, voa- folidine° (iso-v.°), voafoleine° (iso-v.°).

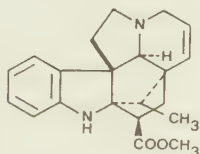
P6a

venalstonine

alkaloid Ld 65 (a.-Ld 85), aspidofiline, aspidofractine, aspidofractinine (11,12-dimethoxy-a.; N-formyl-11,12-dimethoxy-a.; N-formyl-12-methoxy-a.; 12-methoxy-a.), kopsaporine, kopsingine,

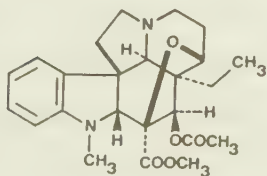
Table 20. Cont'd

<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>P6a</u> cont'd		
	kopsinilam, kopsininē (14,15-dehydro-5-oxo-k.; epoxy-k.; 15-hydroxy-k.; 19-hydroxy-k.; k.-N-oxide), kopsinic acid methochloride, maidinine, pleiocarpine (5,6-dioxo-p.), pleiocarpinilam, pleiocarpinine, pleiocarpoline, pleiocarpolinine, pyrifoline, pleiomutine°, refractidine, refractine, venalstonidine, venalstonine.	

P6b

vindolinine

pleiomutinine°, pseudokopsinine (p.-N-oxide), pycnanthine° (14',15'-dihydro-p.°), tuboxenine (epi-t.), vindolinine (19-epi-v.; 19-epi-v.-N-oxide; v.-N-oxide).

P6c

cathovaline

cathanneine, cathovaline (des-acetyl-c.; 14-hydroxy-c.).

Table 20. Cont'd

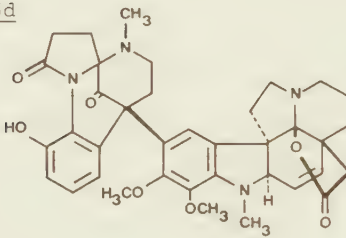
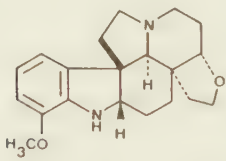
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>P6d</u>		aspidoalbidine (N-acetyl-a.; N-acetyl-12-methoxy-a.; N-formyl-12-methoxy-a.), aspidoalbine (N-acetyl-N-depropionyl-a.; 18-oxo-a.; 18-oxo-O-methyl-a.), aspido-fendlerine, aspidoalimidine (N-propionyl-N-desacetyl-a.), cimicidine, cimicine, cimiciphytine (nor-c.), dichotamine, fendlerine haplocidine, haplocine, haplophytine.
<u>P6e</u>		amataine°, apodine (desoxo-a.), beninine (1,2-dehydro-b.), calli-chiline°, folicangine°, goziline°, hedrantherine (12-hydroxy-h.), owerreine°, quimbeline°, subsessi-line-lactone°, voafolidine° (iso-v.), voafoline° (iso-v.), vobtusine° (12-O-demethyl-v.; desoxy-v.; 2-desoxy-v.-lactam°; desoxy-v.-lactone°; v.-3-lactam°; v.-3-lactam-N-oxid°, v.-lactone°).

Table 20. Cont'd

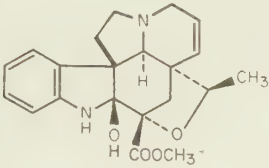
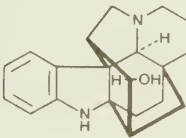
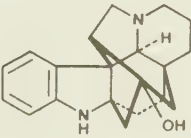
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>P6f</u>		melobaline, vincoline.
melobaline		
<u>P7a</u>		N-carbomethoxy-5,22-dioxo-kopsan, 5,22-dioxo-kopsan, kopsanol (22-epi-k.; N-formyl-k.; 5-oxo-16-epi-k.), kopsanone, kopsine (decarbomethoxy-k.), N-methyl-5,22-dioxo-k.
kopsanole		
<u>P7b</u>		decarbomethoxy-isokopsine.
decarbomethoxy-isokopsine		

Table 20. Cont'd

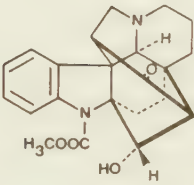
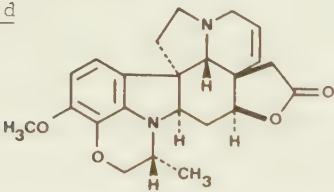
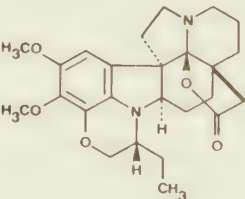
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>P7c</u>		fruticosamine, fruticosine.
<u>P7d</u>		neblinine, obscurinervidine (di-hydro-o.), obscurinervine (di-hydro-o.).
<u>P7e</u>		alalakine.

Table 21. Numbers of isolations of indole alkaloids of
plumeran(P)-type

	species	Skeleton types									P-types
		<u>P3</u>	<u>P4</u>	<u>P5</u>	<u>P6a</u>	<u>P6b</u>	<u>P6d</u>	<u>P6e</u>	<u>P7a</u>	other	
<u>APOCYNACEAE</u>											
<u>Plumerioideae</u>											
<u>CARISSEAE</u>											
<i>Hunteria</i>	2	2	1	5	8						
<i>Melodinus</i>	5		2	26	12	6				<u>P6f</u> :1	
<i>Pleiocarpa</i>	3		1	2	27	3			3		
<u>TABERNAEMONTANEAE</u>											
<i>Callichilia</i>	2								8		
<i>Conopharyngia</i>	2		1	1					2		
<i>Crioceras</i>	2		2	2					2		
<i>Ervatamia</i>	3		1	9							
<i>Hazunta</i>	1			2							
<i>Hedranthera</i>	1		1						16		
<i>Pagiantha</i>	1		1								
<i>Pandaca</i>	2		1	2							
<i>Rejoua</i>	1								1		
<i>Stemmadenia</i>	3		1	3							
<i>Stenosolen</i>	1			1							
<i>Tabernaemontana</i>	4		2	10					2		
<i>Tabernanthe</i>	1		1								
<i>Voacanga</i>	9		3	7					54		
<u>ALSTONIEAE</u>											
<i>Alstonia</i>	1			6	3						
<i>Amsonia</i>	3	14	7	14							
<i>Aspidosperma</i>	38		8	93	15		17		20	<u>P7d</u> :5; <u>P7e</u> :1	
<i>Catharanthus</i>	5			54	4	5				<u>P6c</u> :5; <u>P6f</u> :1	
<i>Craspidospermum</i>	2			2	2						
<i>Geissospermum</i>	1			4							
<i>Gonioma</i>	2		2	2	1	1					
<i>Haplophyton</i>	1							7			
<i>Rhazya</i>	2	19	2	5							
<i>Vinea</i>	7		7	27	8	2				<u>P6f</u> :1	
<u>RAUVOLFIEAE</u>											
<i>Cabucala</i>	2			3							
<i>Kopsia</i>	4				3				4	<u>P7b</u> :1; <u>P7c</u> :2	
<i>Vallesia</i>	2		1	8			5				

Table 22. Distribution of alkaloids of plumeran(P)-type in plant families

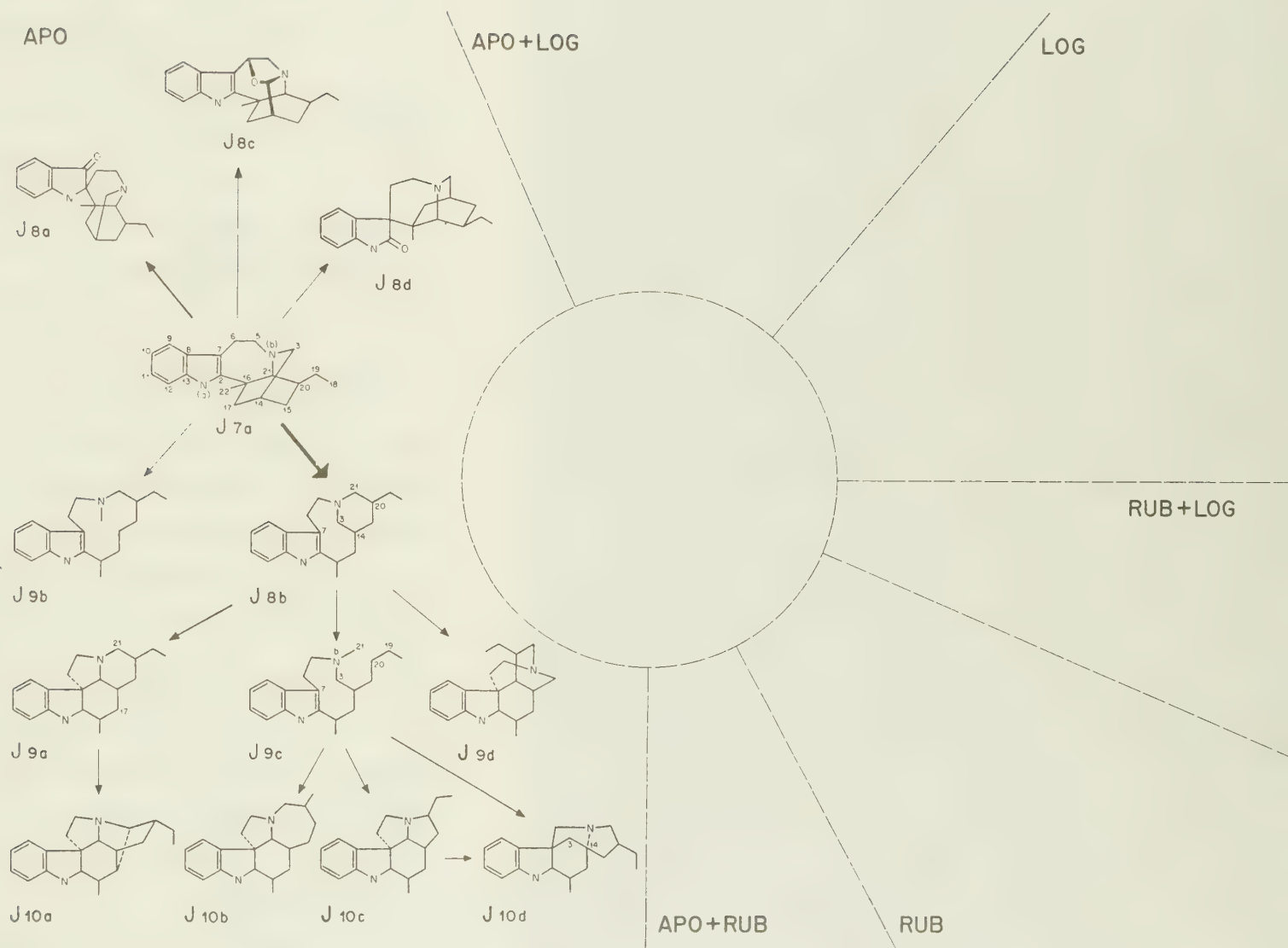
Family	LOGANIACEAE	APOCYNACEAE	RUBIACEAE
Subfamily		PLUMERIOIDEAE	CINCHONOIDEAE RUBIOIDEAE GUETTARDOIDEAE
Tribe	GEL STR	CAR TAB ALS RAU	NAU CIN MUS PSY URO GUE
Number of genera		3 14 10 3	
Number of species		10 33 62 8	
		Number of isolations	627
		with absolute configuration	415 = 66%
		Number of structurally different alkaloids	283

2.8. Alkaloids of ibogan(J)-type

The main skeleton type is J7a (e.g. conopharyngine) (scheme 12). Oxidation at C(7) or at C(2) in J7a leads to J8a (e.g. iboluteine) and respectively to J8d (e.g. crassanine). On the other hand, an oxidative cyclisation between C(3)-OH and C(6) yields J8c (e.g. eglandine). From the cleavage of the bond C(16)-C(21) J8b (e.g. dihydro-cleavamine) is formed, which can also be derived from P3 as demonstrated in scheme 2. In J8b, the cleavages of the bonds C(3)-C(14) or C(20)-C(21) lead to the formation of J9b (e.g. catharine) and of J9c (e.g. catharinine) respectively, of which the later can undergo another cyclisation [C(19)-C(21)] following a new bond formation C(3)-C(7) to result in J10b (e.g. iboxyphyllidine). Also in J9c, a N-deformylation of C(21) followed by a new bonding of N(b)-C(20) provides the skeleton type J10c (e.g. ibophyllidine). From J8b, by a new bond formation C(3)-C(7), J9a (e.g. pandoline) can be produced from which by an additional reaction step (formation of the bond C(17)-C(21)) J10a (e.g. pandine)

can be derived. By similar complex reactions J9d (e.g. vincathicine) and J10d (e.g. ervafoline) can be explained. For some of the mentioned reaction sequences, there can be other conceivable alternatives. The representative examples of the ibogan-group with the names of the isolated alkaloids belonging to each of skeleton types are given in table 23.

Botanical source of the ibogan alkaloids is also confined to the subfamily Plumerioideae of Apocynaceae as illustrated in table 24 and 25.



Scheme 12.¹⁰ Distribution of alkaloids of ibogan (J)-type in plant families.

Table 23. Ibogan (J)-type - examples of structure

and names of all isolated alkaloids

($^{\circ}$ = bisindole alkaloid, given twice if necessary)

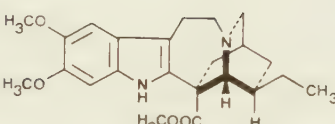
Types	Example	Alkaloids
J7a		bis-(11-hydroxy-coronaridiny1)- 12 $^{\circ}$, bonafousine, catharanthine, conoduramine $^{\circ}$ (19,20-epoxy-c. $^{\circ}$), conodurine $^{\circ}$ (19-oxo-c. $^{\circ}$), cono- pharyngine (19-hydroxy-c.; 3-oxo- c.), coronaridine (19-hydroxy-c.; hydroxyindolenine-c.; 19-hydroxy-
	conopharyngine	3-oxo-c.; 3-oxo-c.; 19-oxo-c.), eglandulosine, 19-epi-iboxygaline, gabunamine $^{\circ}$, gabunine $^{\circ}$, heyneanine (19-epi-h.), ibogaine (hydroxy- indolenine-i.), ibogaline, ibogamine (20-epi-i.; hydroxyindole- nine-i.), iboxygaine (19-epi-i.; hydroxyindolenine-i.), jolly- anine, tabernaelegantine A $^{\circ}$ (t-B $^{\circ}$; t-C $^{\circ}$; t-D $^{\circ}$), tabernaeleganti- nine A $^{\circ}$ (t-B $^{\circ}$), tabernamine $^{\circ}$, tabernanthine, voacamidine $^{\circ}$, voa- camine $^{\circ}$ (16-decarbomethoxy-dihydro-v. $^{\circ}$; 16-decarbomethoxy-20'- epi-dihydro-v. $^{\circ}$; 18'-decabomethoxy-v. $^{\circ}$; N-demethyl-v. $^{\circ}$; v.-N- oxide $^{\circ}$), voacangine (hydroxyindolenine-v.; 3-hydroxy-iso-v.; 6-hydroxy-3-oxo-iso-v.; iso-v.; 3-oxo-v.; v.-lactam), voacorine $^{\circ}$ (19-epi-v. $^{\circ}$), voacristine (19-epi-v.; hydroxyindolenine-v.; iso-v.), voacryptine.

Table 23. Cont'd

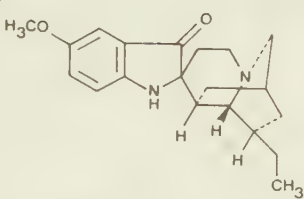
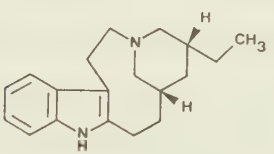
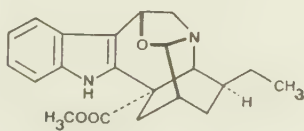
Type	Example	Alkaloids
J8a	 ibololuteine	conopharyngine-pseudoindoxyl, coronaridine-pseudoindoxyl, ibololuteine (demethoxy-i.), rupicoline, voacangine-pseudoindoxyl, voacristine-pseudoindoxyl, voaloluteine.
J8b	 7R-dihydro-cleavamine	capuvosine° (15-dehydroxy-c.°; N-demethyl-c.°), capuronine, 20R-dihydro-cleavamine (20S-dihydro-c.), leurocolombine°, leurocristine°, leurosidine°, leurosine° (iso-l.°), pleurosine°, pseudo-vincaleukoblastine-diol°, vinblastine° (desacetoxy-v.°), vincovalicine°, vincovaline°, vincovalinine°.
J8c	 eglandine	eglandine, 3,6-oxido-isovoacangine

Table 23. Cont'd

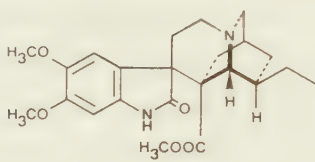
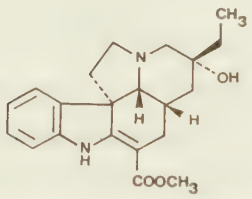
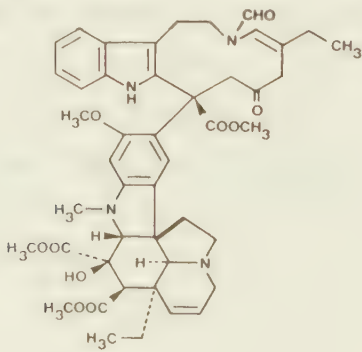
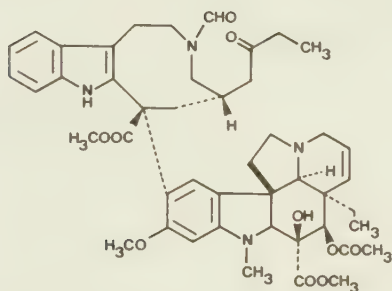
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>J8d</u>		crassanine, kisanine.
<u>J9a</u>		capuvosidine°, capuronidine (14,15 anhydro-c.; 14,15-anhydro-1,2-dihydro-c.), 20S-1,2-dehydro-pseudo-aspidospermidine, pandoline (20-epi-p.), pseudotabersonine, 20R-pseudovincadifformine.
<u>J9b</u>		catharine°.
	catharine	

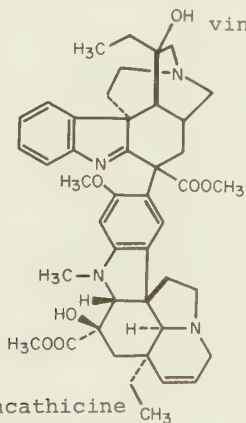
Table 23. Cont'd

<u>Type</u>	<u>Example</u>	<u>Alkaloid</u>
<u>J9c</u>		catharinine°.



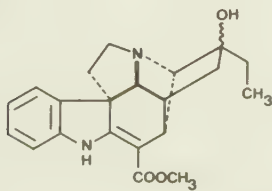
catharinine

<u>J9d</u>		vincathicine°.
------------	--	----------------



vincathicine

<u>J10a</u>		pandine.
-------------	--	----------



pandine

Table 23. Cont'd

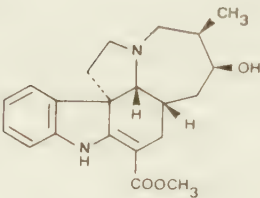
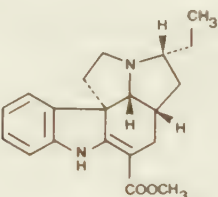
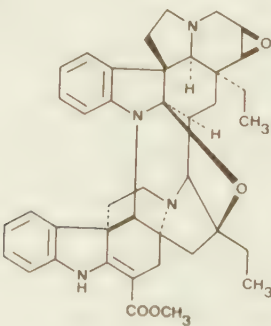
<u>Type</u>	<u>Example</u>	<u>Alkaloids</u>
<u>J10b</u>		iboxyphylline.
<u>J10c</u>		ibophyllidine.
<u>J10d</u>		ervafolidine° (iso-e.°), ervafoline°.

Table 24. Number of isolations of indole alkaloids of
ibogan(J)-type

species	Skeleton types												
	J7a	J8a	J8b	J8c	J8d	J9a	J9b	J9c	J9d	J10a	J10b	J10c	J10d
<u>APOCYNACEAE</u>													
<u>Plumerioideae</u>													
<u>CARISSEAE</u>													
<i>Melodinus</i>	2	2				2							
<u>TABERNAEMONTANEAE</u>													
<i>Anacampta</i>	1		2										
<i>Bonafousia</i>	1	6											
<i>Capuronetta</i>	1			4		4							
<i>Conopharyngia</i>	10	53	1		1								
<i>Ervatamia</i>	6	18				2							3
<i>Gabunia</i>	2	14		1									
<i>Hazunta</i>	7	14											
<i>Hedranthera</i>	1	2											
<i>Muntafara</i>	1	4		2									
<i>Pagiantha</i>	3	11	1										
<i>Pandaca</i>	11	30	2	2		7				2			
<i>Peschiera</i>	6	21	2										
<i>Rejoua</i>	1	1	2										
<i>Stemmadenia</i>	4	9											
<i>Stenosolen</i>	1												1
<i>Tabernaemontana</i>	5	18											
<i>Tabernanthe</i>	2	12	2		1						2	2	
<i>Voacanga</i>	6	28	3										
<u>ALSTONIEAE</u>													
<i>Alstonia</i>	1	1											
<i>Catharanthus</i>	4	6	15				4	3	1				

Table 25. Distribution of alkaloids of ibogan(J)-type in plant families

Family	LOGANIACEAE	APOCYNACEAE	RUBIACEAE				
Subfamily		PLUMERIOIDEAE	CINCHONOIDEAE	RUBIOIDEAE	GUETTARDOIDEAE		
Tribe	GEL STR	CAR TAB ALS RAU	NAU CIN MUS	PSY URO	GUE		
Number of genera	1 18 2						
Number of species	2 69 5						

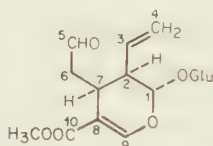
Number of isolations	324
with absolute configuration	184 = 57%
Number of structurally different alkaloids (bisindole alkaloids are counted twice)	109

3. Absolute configuration of indole alkaloids containing a C₉- or C₁₀-monoterpene moiety.

As already mentioned in the foregoing discussion, of all the isolations of indole alkaloids containing a C₉- or C₁₀-monoterpene moiety, only approximately 46% could also be determined in their absolute configuration, since the indications about special properties were completely or partly missing in some of the publications or the absolute configuration of some alkaloids are still unknown. With respect to the expressions used for absolute configuration in this paper, namely α and β , it is recommended to see scheme 2. As demonstrated in scheme 3, the main skeleton types of indole alkaloids can biogenetically be divided into two groups : the corynanthean (C)-, vincosane (D)-, vallesiachotamine (V)-, strychnine (S)- and aspidospermatine (A)-types containing a skeleton with a non-rearranged secologanin moiety and the eburnane (E)-, plumerane (P)- and ibogane (J)-types with a rearranged secologanin moiety. This classification is confirmed, in addition to the common structural features, also by the fact that all of the C-, D-, V-, S- and A-type alkaloids - with known absolute configuration - show the same absolute configuration at C(15) as secologanin (ae)¹⁴ at C(7).

-
- 14) C(7) of secologanin corresponds to C(15) of the indole alkaloids being discussed. The natural (-)-secologanin has the same absolute configuration at this C-atom as the mentioned indole alkaloids.

Being based on 935 isolations of alkaloids with known absolute configuration and belonging to the five groups of skeleton types, this statement should convincingly be regarded as representative.



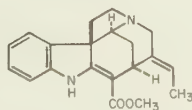
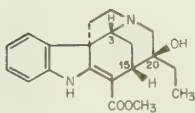
ae, (-)-secologanin

However, while searching for alkaloid isolations of A-, D-, C-, S- and A-types in the literature, we were confronted with four exceptions, which have the opposite configuration of that of (-)-secologanin :

- a) In the first case, (-)-quebrachidine (type C5c) isolated from *Cabucala erythrocarpa* var. *erythrocarpa* (Vatke) Mgf. (18), it turned out to be a misprint and has been confirmed to be in fact (+)-quebrachidine as expected (19).
- b) The second exception, which unfortunately could not be checked, is presented by a remote isolation of (-)-yohimbine (type C4b) from *Rauvolfia canescens* L. (20), though yohimbine isolated very frequently, shows

a $[\alpha]_D$ value of $+80^\circ$ to 100° in pyridine. However, since *R. canescens* L. is botanically identical with *R. hirsuta* Jacq, *R. heterophylla* R. et S., *R. tetraphylla* L., and also a (+)-yohimbine has been isolated from *R. heterophylla* L., it should be accepted that exclusively (+)-yohimbine occurs naturally and the mentioned (-)- $[\alpha]_D$ value should necessarily have been a mistake.

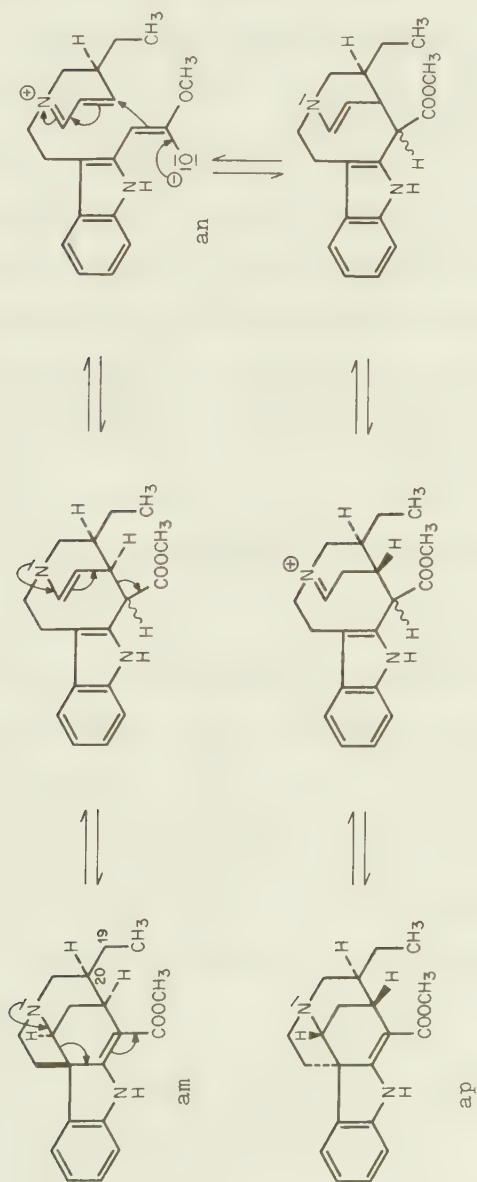
- c) The later two of the mentioned four exceptional cases are the strychnan type alkaloids : (+)-20-epi-lochneridine (type S4) (ak) isolated from *Ervatamia pandacaqui* (Poir.)Pich ($\equiv$ *Tabernaemontana pandacaqui* Poir.) (17) should be assigned to the β -group considering its absolute configuration, and pseudoakuammicine ($\equiv$ (+)-akuammicine) isolated from *Picralima nitida* (Stapf) Dur. ($\equiv$ *P. klaineana* Pierre) (22, 23) with $[\alpha]_D = 0$ represents a mixture of (+)- and (-)-akuammicine (type S4) (al) possessing α - as well as β -configuration.



ak, (+)-20-epi-lochneridine al, (-)-akuammicine

On this finding, it is a striking fact that both of the alkaloids (+)-20-epi-lochneridine (ak) and (-)-akuammicine contain a β -anilino-acryl ester chromophor. Recently, it could be shown on the basis of a model-experiment that exhaustive heating (95°/50 h) of (-)-19,20-dihydro-akuammicine in absolute CH₃OH yields a mixture of diastereomers (-)-19,20-dihydro-akuammicine (am) and (+)-20-epi-19,20-dihydro-akuammicine (ap) (ratio ca. 4:1) (24). According to the proposed mechanism (scheme 13), the chiral centers 3, 7 and 15 can be racemised. The ratio of [am]/[ap] is determined by the center 20 in an which is also chiral.

Scheme 13. Isomerisation of 19,20-dihydro-akuammicine.



However, if there is no additional center of chirality available in the starting molecule, a racemate is formed after the equilibrium has been attained, e.g. akuammicine (al). On the other hand, the presence of an other chiral center (for example C(20) in 19,20-dihydro-akuammicine (am), 20-epi-lochneridine (ak)) leads to a mixture of diastereomers, the composition of which can not be predicted a priori. Even if the reaction under the previously mentioned conditions definitely can not take place in vivo, there are some hints indicating the possibility for racemisation during the extraction or in the plant under modified conditions. Hence, it seems plausible that the β -configuration of (+)-20-epi-lochneridine (ak) and (+)-akuammicine does not need to be explained by a primary biogenetic step. The original configuration in both of these cases is very probably also α .

The skeleton type A5b as mentioned before is misplaced within the A-types. From biogenetical reasons it would be more plausible to combine it with the P-types, see chapter 2.5. The alkaloids containing a rearranged secologanin moiety (E-, P-, and J-types) do not present a uniform characteristic in common, with respect to their configurations, as it was the case by the alkaloids with non-rearranged secologanin moiety.

The plumeran alkaloids discussed recently (2) in a separate report show α - as well as β -configuration ($\alpha/\beta = 1/1,5$).

The skeleton types P4 and P5, to which the majority of alkaloids belong, occur as antipodial skeletons and are therefore α - as well as β -configured. Among the skeleton types derivable from P5, P6a, P6b, P6e, P6f occur only α -configured, while P6d and P7d have only the β -configuration (scheme 11). The skeleton type P7a which can be derived from P6a occurs also α -configured as its precursor. Obviously, the plant enzymes essential for the formation of the alkaloids belonging to the skeleton types P6 and P7 are so specific that only representatives of one certain configuration can be synthesized.

The rearrangement of the secologanin moiety (scheme 3) does not seem to show any specific character with respect to the configuration at C(7) in ae. It should be mentioned that alkaloids of α - and β -plumeran group does occur in the same plant species together. Therefore, the heterogeneity of the absolute configuration of plumeran alkaloids does not seem to be a function of the synthesizing plants; it can rather be correlated with skeleton types.

The other alkaloids with a rearranged secologanin moiety, namely those of eburnan (E)- and ibogan (J)-types, also do not show an uniform picture with respect to their absolute configuration. Alkaloids of eburnan skeleton (scheme 10) are α -configured, if they have a methoxycarbonyl group at C(16); whereas the β -configuration emerges, if the same center C(16) is substituted either with two hydrogen atoms or one oxygen in form of a keto- or hydroxy-group. However, this observed regularity is contradicted with exceptions: (+)-vincamine and (+)-16-epi-vincamine (skeleton type E5a with C(16)-COOCH₃) isolated from *Anacampta rigida* Mgf. (= *Tabernaemontana rigida* (Miers,) Mgf.) and (+)- and (+)-eburnamonine (skeleton type E5a with C(16)=O) isolated from *Vinca minor* L. So far, a reasonable explanation for these cases could not be established.

Within the ibogan group, in which all of the compounds, so far, have been found as β -configured, we also met two exceptions in skeleton type J7a : (+)-catharanthine (α -configured, isolated from *Catharanthus* species) and (+)-ibogamine (isolated from *Pandaca retusa* Mgf.). It seems important to note, that only the basic skeletons E5a, P4, P5 and J7a of the rearranged secologanine alkaloids are known to occur in nature as racemates or

antipodal skeletons. The more complex alkaloids of each type possess only one absolute configuration, α or β depending on the special skeleton type.

The occurrence of the alkaloids of all skeleton types with their corresponding absolute configurations is demonstrated in table 26, so that the uniformity can clearly be recognized again. Alkaloids with a non-rearranged secologanin moiety, exclusively, are α -configured, whereas those with a rearranged secologanin moiety have α - and β -configuration.

Table 26. Isolations and absolute configuration of indole alkaloids with a C_9 - or C_{10} -monoterpene moiety

plant families	Skeleton types							
	with non-rearranged secologanin part					with rearranged secologanin part		
	C	D	V	S	A	E	P	J
APO	1089	19	15	51	58	86	627	324
abs. conf.	α					$\alpha + \beta$		
LOG	104	2	49	356	1	-	-	-
abs. conf.	α							
RUB	608	37	23	-	-	-	-	-
abs. conf.	α							

4. Results and discussion

4.1. Differentiation of Apocynaceae, Loganiaceae and Rubiaceae with respect to the structure types of indole alkaloids.

More than 99.8% of the isolations of the indole alkaloids classified in eight skeleton types - five of them with a non-rearranged secologanin moiety and three with a rearranged one - are entirely distributed among three plant families : Apocynaceae, Loganiaceae and Rubiaceae. The evident detections and identifications of indole alkaloids discussed in 64 genera and 426 species of these three plant families gave us the impression that it would be worth attempting a study in respect of chemotaxonomy in order to check, or eventually to modify the botanical classification. The occurrence of alkaloids belonging to the skeleton types discussed in the three mentioned plant families is summarized in table 27.

Only the alkaloids of C-, D- and V-types have been detected in all of the three families. Especially, the number of isolations of corynanthean alkaloids permits a conceivable argumentation with respect to chemotaxonomy (Apocynaceae = 1089, Loganiaceae = 104 and Rubiaceae = 608). Also considering the absolute configuration, which is exclusively α , identical to that of the natural secologanin (ae), in case of C-, D- and

Table 27. Occurrence of indole alkaloids in *Apocynaceae*, *Loganiaceae*
and *Rubiaceae*

	No.of investi- gated species	with non-rearranged secologanin part					with rearranged secologanin part			
		C	D	V	S	A	E	P	J	total
<i>APOCYNACEAE</i>										
<i>Plumerioideae</i>										
<i>CARISSEAE</i>	16	64	4	7	7	5	17	100	4	208
<i>Hunteria</i>	4	33		5	2		7	16		
<i>Melodinus</i>	6	5				4	4	47	4	
<i>Pieralima</i>	1	10			2					
<i>Pleiocarpa</i>	5	16	4	2	3	1	6	37		
<i>TABERNAEMONTANEAE</i>	90	199	1		4	13	27	136	290	669
<i>Anacampta</i>	2						7		2	
<i>Bonafousia</i>	1	1							6	
<i>Callichilia</i>	2							8		
<i>Capuronetta</i>	1	4							8	
<i>Conopharyngia</i>	10	29				2		4	55	
<i>Crioceras</i>	2						9	6		
<i>Ervatamia</i>	7	17			1			10	23	
<i>Gabunia</i>	2	9							15	
<i>Hazunta</i>	9	34			2	1		2	14	
<i>Hedranthera</i>	1	2						17	2	
<i>Muntafara</i>	1	2							6	
<i>Pagiantha</i>	4	3						1	12	
<i>Pandaca</i>	13	11			1	6	1	3	43	
<i>Peschiera</i>	7	30							23	
<i>Rejoua</i>	1							1	3	
<i>Schizosygia</i>	1						7			
<i>Stemmadenia</i>	4	2				3		4	9	
<i>Stenosolen</i>	1							1	1	
<i>Tabernaemontana</i>	9	8				1		14	18	
<i>Tabernanthe</i>	2							1	19	
<i>Voacanga</i>	10	47	1				3	64	31	

Table 27. Cont'd

	No.of investi- gated species	with non-rearranged secologanin part					with rearranged secologanin part			total
		C	D	V	S	A	E	P	J	
<u>APOCYNACEAE</u>										
<u>Plumerioideae</u>										
<u>ALSTONIEAE</u>	91	326	5	6	39	34	41	364	30	845
<i>Alstonia</i>	17	107	1		12	2		9	1	
<i>Amsonia</i>	3	12		3	2	1	7	35		
<i>Aspidosperma</i>	44	65			1	21	4	159		
<i>Catharanthus</i>	6	33	2	1	7	1	1	69	29	
<i>Craspidospermum</i>	2					6	4	4		
<i>Diplorrhynchus</i>	1	3			2	2				
<i>Geissospermum</i>	3	5			4	1		4		
<i>Gonioma</i>	2	4					1	6		
<i>Haplophyton</i>	1						3	7		
<i>Rhazya</i>	2	7	2	2	2		3	26		
<i>Tonduzia</i>	1	6								
<i>Vinea</i>	9	84			9		18	45		
<u>RAUVOLFIEAE</u>	76	500	9	2	1	6	1	27		546
<i>Cabucala</i>	5	38			1			3		
<i>Kopsia</i>	4							10		
<i>Neisosperma</i>	6	27								
<i>Ochrosia</i>	10	25		1						
<i>Rauwolfia</i>	49	407	9							
<i>Vallesia</i>	2	3		1		6	1	14		
<u>APOCYNACEAE / total</u>	273	1089	19	15	51	58	86	627	324	2269

Table 27. Cont'd

	No. of investi- gated species	with non-rearranged secologanin part					with rearranged secologanin part		
		C	D	V	S	A	E	P	J
<u>RUBIACEAE</u>									
<u>Cinchonoideae</u>									
<u>NAUCLEEAE</u>									
<i>Adina</i>	2	4	10	4					
<i>Anthocephalus</i>	1		8						
<i>Cephalanthus</i>	1	6							
<i>Mitragyna</i>	10	119		2					
<i>Nauclea</i>	2		6	1					
<i>Neonauclea</i>	1	1							
<i>Sarcocephalus</i>	2		2	7					
<i>Uncaria</i>	43	432		8					
<u>CINCHONEAE</u>									
<i>Cinchona</i>	3	8							
<i>Corynanthe</i>	3	18							
<i>Pausinystalia</i>	3	16							
<i>Remijia</i>	1	1							
<u>MUSSAENDEAE</u>									
<i>Isertia</i>	1	2							
<u>Rubioideae</u>									
<u>PSYCHOTRIEAE</u>									
<i>Palicourea</i>	1		1						
<u>UROPHYLLEAE</u>									
<i>Pauridiantha</i>	2		9						
<u>Guettardoideae</u>									
<u>GUETTARDEAE</u>									
<i>Antirhea</i>	1			1					
<i>Guettarda</i>	1	1							
<u>RUBIACEAE / total</u>	78	608	37	23					668

Table 27. Cont'd

	No.of investi- gated species	with non-rearranged secologanin part					with rearranged secologanin part		
		C	D	V	S	A	E	P	J
<i>LOGANIACEAE</i>									
<i>GELSEMIEAE</i>									
<i>Gelsemium</i>	2	2							
<i>Mostuea</i>	2	2							
<i>STRYCHNEAE</i>									
<i>Gardneria</i>	3	24							
<i>Strychnos</i>	68	76	2	49	356	1			
<i>LOGANIACEAE</i> / total	75	104	2	49	356	1			512

V-alkaloids it can reliably be proposed that these skeletons should be the "precursors" of all indole alkaloids with a C_9 - or C_{10} -monoterpene moiety. However, it should be accentuated that the quality is decisive, rather than the quantity : the relatively less abundance of vincosan (D)-, and vallesiachotaman (V)-alkaloids occurring also as α -configured can be explained with the higher reactivity of these compounds leading to the C-type in the plant.

Of the other two skeleton types with a non-rearranged secologanin part, strychnan (S)- and aspidospermatan (A)-alkaloids occur both only in Apocynaceae and Loganiaceae.

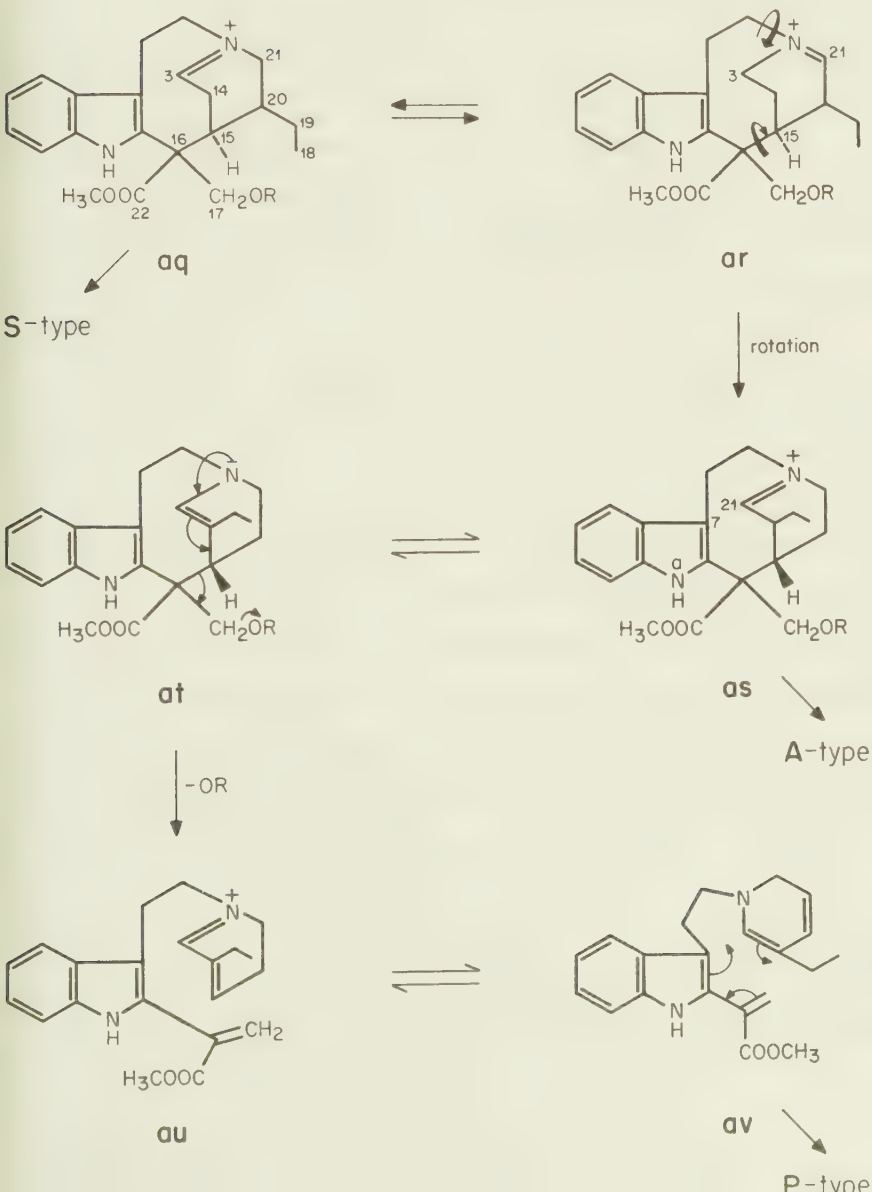
With respect to the skeleton types with a rearranged secologanin moiety, namely eburnan (E)-, plumeran (P)- and ibogan (J)-types, the differences between the three plant families are remarkably greater : only Apocynaceae seems to have the ability to rearrange the secologanin moiety. So far, no alkaloids with a rearranged secologanin moiety have been identified in Loganiaceae and Rubiaceae. Also the alkaloids of aspidospermatan (A)-type do occur mainly in Apocynaceae; only one isolation is known from Loganiaceae. As a further interesting part, in the genera containing aspidospermatan alkaloids, also alkaloids

with rearranged secologanin moiety have been detected (table 27). This observation allows us to assume a very close biogenetic relationship between the non-rearranged aspidospermatan (A)-skeleton and the rearranged skeleton types (E-, P- and J-types). In scheme 14, this relationship is demonstrated : the decisive step seems to be the isomerization $\underline{aq} \rightarrow \underline{ar}$, in which the C(3),N-double bond is transformed to C(21),N-double bond. In this way, the precursor of A-type ($\underline{as}$) which is clearly close to a skeleton with a rearranged secologanin moiety (e.g. P-type, scheme 11) is derived from the precursor of S-type ($\underline{aq}$)

Conclusively, with respect to the occurrence of indole alkaloids with C_9 - or C_{10} -monoterpene moiety, Apocynaceae, producing all of the skeleton variations, should be regarded as the highest "evolved" plant family among the three families being discussed.

For a further differentiation between Loganiaceae and Rubiaceae, another class of alkaloids - also containing a non-rearranged secologanin moiety - provides a convincing criterion : Besides Melodinus (Apocynaceae, Plumerioideae, Carisseae) the Rubiaceae are the only plant family with the ability to rearrange the indole chromophor into a quinoline (e.g. quinine ($\underline{aw}$)). Further, they can condense secologanin with tryamine instead of tryptamine to produce the isoquinoline alkaloids of emetine type

Scheme 14. Biogenetic relationship of aspidospermatan (A)-skeleton with rearranged skeleton types.



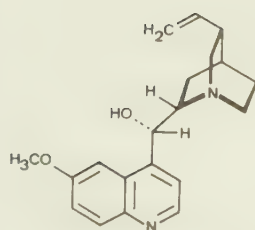
(e.g. emetine, ax). Finally, the alkaloids of tubulosine type (e.g. tubulosine, ay) in which the secologanin is condensed with tryptamine as well as with tyramine, should also be mentioned. All these additional types of alkaloids contain a non-rearranged secologanin moiety and have been detected only in Rubiaceae. Therefore, Rubiaceae are comparable with Apocynaceae regarding the "evolution stage" and both should be placed higher than the Loganiaceae.

4.2. Differentiation of the tribus of Apocynaceae

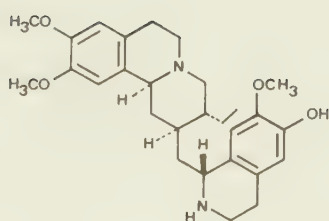
As mentioned previously, the indole alkaloids containing a C₉- or C₁₀-monoterpene moiety do occur only in one subfamily of Apocynaceae, namely in Plumerioideae, and not in the other two subfamilies, Cerberoideae and Echitoideae. Of the seven tribes of Plumerioideae, only four, namely Carisseae, Tabernaemontaneae, Alstonieae and Rauvolfieae contain the indole alkaloids being discussed. So far, of the other three tribes, no results of investigations have been available.

4.2.1. Carisseae

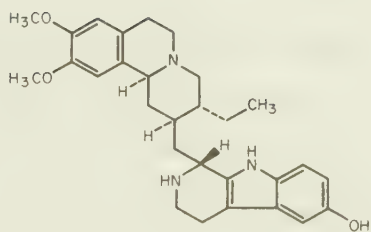
In Carisseae, all of the main skeleton types do occur. Although the isolations are restricted to 16 species,



a.w
quinine



a.x
emetine



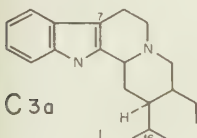
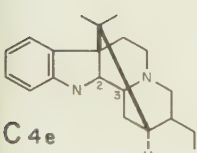
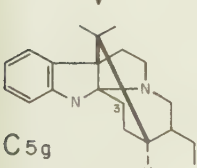
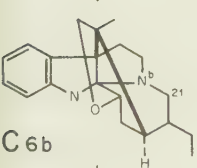
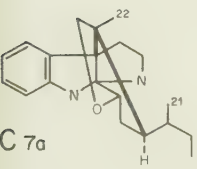
a.y
tubulosine

their number, 208, is remarkable. Also the number of sub-skeleton types, 35 out of the total of 105 skeleton types, is fairly interesting and seems to be typical in the case of *Pleiocarpa* especially.

With the exception of *Picralima*, the three other genera do have the ability to form also the skeleton types with a rearranged secologanin moiety. Only the species of *Melodinus* are able to succeed the second rearrangement leading to the ibogan type.

An especially interesting example of the group of corynanthean alkaloids for the chemotaxonomic approach should be demonstrated : as already mentioned previously, the structurally simple alkaloids are more "wide-spread" than those derived from simple precursors by cyclisations, oxidations etc. In scheme 15 such a "biogenetic row" is demonstrated. As the alkaloids with the C3a skeleton have been detected in all of the plant families under discussion, the alkaloids of C4e type derived from C3a by one additional C,C-bonding do occur only in Apocynaceae. The increasing variation of the molecular structure leads to a impoverishment of the occurrence. Alkaloids of the most complicated skeleton type C8a have been detected only in one species of *Hunteria*. Similar "biogenetic rows" can also be established among other skeleton groups.

Scheme 15. Example of a "biogenetic row".

skeleton type	Occurrence in				LOG STR	RUB	
	CAR	APO TAB	ALS	RAU		NAU	CIN
 C 3a	+	+	+	+	+	+	+
 C 4e	+	+	+	+			
 C 5g	+		+	+			
 C 6b	+						
 C 7a	+						

4.2.2. Tabernaemontaneae

Tabernaemontaneae represents a rather uniform and closed tribe in comparison to those other of Plumerioideae. According to the investigation so far, the indole alkaloids with a C_9 - or C_{10} -monoterpene moiety have been detected in 21 genera and 90 species. The formation of ibogan skeleton types seems to be very suitable for characterization of Tabernaemontaneae-species, since the alkaloids of ibogan type do occur - with the exception of *Alstonia* and *Catharanthus* (Alstonieae) and *Melodinus* (Carisseae) - only in Tabernaemontaneae. Only three of the 13 mentioned genera, namely *Callichilia*, *Crioceras* and *Schizozygia*, do not contain alkaloids of ibogan type. The other alkaloid types containing a rearranged secologanin moiety (E- and P-types) have also been abundantly detected in Tabernaemontaneae. Only low numbers of isolations are attained by the alkaloids with a non-rearranged secologanin moiety (vincosan (D)-, strychnan (S)- and aspidospermatan (A)-types) (table 27). Among 21 genera, *Pandaca* containing alkaloids of all types except D and V shows the greatest variety.

As already mentioned in a foregoing study (2), Tabernaemontaneae shows also an uniformity in the case of plumeran alkaloids. Only the skeleton types P3, P4, P5 and P6e can be formed (scheme 11, table 21). The alkaloids of the special skeleton type P6e, which can be derived from P5 by oxidation, have been detected only in Tabernaemontaneae. The skeleton types - iso- related from Pandaca and Capuronetta species - which were indicated as 4z, 5z and 6z types in a previous study about plumeran alkaloids (2), have been considered (from the biogenetic point of view) within the ibogan alkaloids in this study.

Finally, it is worth of mention, that among 90 investigated Tabernaemontaneae species, Schizozygia coffeoides Baillon deserves a special position, since from this species, only alkaloids of a specific eburnan skeleton type E6a have been isolated.

Generally, it can be ascertained that among all of the skeleton types, those derived from basic type by oxidative processes were the most frequently isolated ones. In this context, especially two skeleton types should be mentioned: P6e (derived from P5) with 85 isolations and C5a (inclusive C6c; derived from C4c) with 142 isolations (tables 3 and 21). On the other hand, the skeleton type C4b occurring very abundantly in the other three tribes is nearly absent in the species of Tabernaemontaneae (only in Voacanga present).

4.2.3. Alstonieae

Within 845 isolations from 91 species of 12 genera, Alstonieae form one of the most intensively investigated tribe of Apocynaceae. With respect to the main alkaloid types, Alstonieae are considerably less uniform than Tabernaemontaneae, since alkaloids of all the main skeleton types could have been isolated from their species. However, corynanthean (C)- and plumeran (P)-alkaloids have the greatest abundance. Regarding these two main skeleton types Alstonieae present also the largest variety. With the exceptions of Craspidospermum and Haplophyton, the corynanthean skeleton types do occur in all of the investigated genera. In Alstonieae, alkaloids with ibogan skeleton were isolated only from Alstonia and Catharanthus species. Considering the content on ibogan alkaloids, the genera Catharanthus and Vinca differ from each other clearly, based on the evidence that Vinca species do not contain ibogan alkaloids. As already commented in a previous chemotaxonomic study (2), there is another chemotaxonomically remarkable difference between these two genera as bisindole alkaloids could be isolated from the species of Catharanthus, Vinca species contain only "monomeric" bases.

Although *Catharanthus* and *Vinca*, base upon the morphological evidences, should be counted among *Alstonieae*, and not *Tabernaemontaneae*, it should not be concealed that there exist some hints in the direction to *Tabernaemontaneae* : occurrence of ibogan skeleton types - which are distinctly characteristic for *Tabernaemontaneae* in *Catharanthus* and occurrence of the skeleton type C5a in *Tabernaemontaneae*, *Catharanthus* and *Vinca*.

4.2.4. Rauvolfieae

So far, 76 species from 6 genera of *Rauvolfieae* have been investigated.

With the exception of ibogan type, all alkaloids of the main skeleton types do occur in *Rauvolfieae*. However, aside from corynanthean alkaloids (500 isolations), the number of isolations of other types is low. Plumeran type with 27 alkaloid isolations is a little more abundant (table 27).

The genus *Kopsia* containing only plumeran alkaloids of the "most complicated" skeleton type P7b/c (2) rather deserves a special position. *Rauvolfia* containing only alkaloids of corynanthean and vincosan type, *Neisosperma* only corynanthean and *Ochrosia* only corynanthean and vallesiachotaman type are, on the other hand, other genera with special positions.

4.3. Rubiaceae

Rubiaceae with approximately 500 accepted genera and about 6000 species is one of the three plant families containing the indole alkaloids with a C_9 - or C_{10} -monoterpene moiety. Also botanically, Rubiaceae provide sufficient evidences to indicate a close congeniality with Apocynaceae and Loganiaceae. The latest detailed botanical classificaiton of the Genera of Rubiaceae originates from K. Schumann. Later, especially C. Bremekamp and B. Verdcourt accomplished decisive contributions to the classification of this plant family. Regarding the chemotaxonomy of indole alkaloids, we will base our discussion of Rubiaceae on the two recent classifications systems, one of Leeuwenberg (7) and the other of Ehrendorfer. (In the foregoing tables, Rubiaceae are classified according to Leeuwenberg).

4.3.1. Classification of Leeuwenberg (7)

According to the classification of Leeuwenberg (7), Rubiaceae are classified in four subfamilies, namely Rubioideae, Cincho-noideae, Guettardoideae and Hillioideae (table 1). In Rubiaceae, as also in Gelsemieae of Loganiaceae only alkaloids containing a non-rearranged secologanin moiety (corynanthean (C)-, vincosan (D)-, and vallesiachotaman (V)-types) have been detected, by which the corynanthean alkaloids - with 608 isolations from the species of this family - are the most abundant ones (table 27).

On the basis of the classification of Leeuwenberg (7), the occurrence of the indole alkaloids of corynanthean (C)-, vincosan (D)- and vallesiachotaman (V)-types is remarkably concentrated in the subfamily Cinchonoideae (the tribes Naucleae and Cinchoneae) though it should be mentioned that only *Palicourea* and *Pauridiantha* of Rubioideae containing exclusively vincosan (D)-type alkaloids; only *Isertia* of Mussandae containing compounds of C₄g type and *Antirhea* and *Guettarda* of Guettardoideae containing only one alkaloid each of vallesiachotaman(V)- and corynanthean(C)-type rather represent exceptional cases, about which reasonable botanical arguments do seem difficult.

In the subfamily Cinchonoideae, the tribe Cinchoneae being the only one which contains the indole alkaloids with a non-rearranged secologanin moiety as well as quinolin- and isoquinolin type of alkaloids seems to have the basic position for further evolution on Rubiaceae as proposed by Ehrendorfer (25).

In Cinchoneae, while corynanthean (C)-type alkaloids have been detected in the species of *Cinchona*, *Remijia*,

Corynanthe, Pausinystalia; Remijia-, Capirona- and Ferdinandusa-species contain isoquinoline alkaloids of emetine type and Cinchona-, Ladenbergia-, Remijia- and Contarea-species quinoline alkaloids of quinine type, which do occur only in Cinchoneae. The alkaloidal content of the next tribe Naucleaeae is remarkably restricted to the indole alkaloids of all the mentioned types having been detected in Rubiaceae so far, namely of corynanthean (C)-, vincosan (D)- and vallesiachotaman (V)-types (table 3, 6 and 9). The absence of quinoline and isoquinoline alkaloids, as well as the occurrence of indole alkaloids in an increased variety in Naucleaeae compared with Cinchoneae provide a chemotaxonomic basis to differentiate these two tribes. Within the Naucleaeae, the genera Mitragyna and Uncaria attract a special notice by containing, exclusively, alkaloids of the same corynanthean (C)- and vallesiachotaman (V)-types. On the other hand, these two genera are remarkably characterized by occurrence of oxindole alkaloids of C5b-type (scheme 3), a fact which convincingly supports Ehrendorfer in his proposal (25) to classify Mitragyna and Uncaria as a distinct tribe : Mitragyneae. Cephalanthus and Anthocephalus classified also by Ehrendorfer as a separate tribe (Cephalantheae) contain only alkaloids of cory-

nanthean (C)- and vincosan (D)- types. Compounds of C3- and C4d-types have been detected in *Cephalanthus* whilst *Anthocephalus* contain alkaloids of C4a-, D4a-, D4d- and D5a-types among which those of the last two types with a restricted occurrence to this genus. In *Mussaendeae*, alkaloids of the type C51 - which is characteristic for *Cinchona*-species - have been detected in the *Isertia*-species. From the species of *Pogonopus* (*Rondeletieae*) and *Tocoyena* (*Gardenieae*), only isoquinoline alkaloids of emetine type have been isolated so far.

In *Rubioideae*, besides *Palicourea* (*Psychotrieae*) and *Pauridiantha* (*Urophyllaeae*) containing exclusively vincosan (D)-alkaloids, only isoquinoline alkaloids of emetine type have so far been detected : in *Psychotria* and *Cephaelis* of *Psychotrieae*; *Bothiospara* of *Hamelieae*; *Barreria*, *Spermacoce* and *Richardsonia* of *Spermacoceae*, and *Manettia* of *Hedyotideae*.

Within the forth subfamily *Rubiaceae*, *Hillioideae*, only *Hillia* (*Hillieae*) species contain emetine type alkaloids.

4.3.2. Classification of Ehrendorfer (25).

The genera which are of interest for the task of this study and their classification are given in table 1¹⁵.

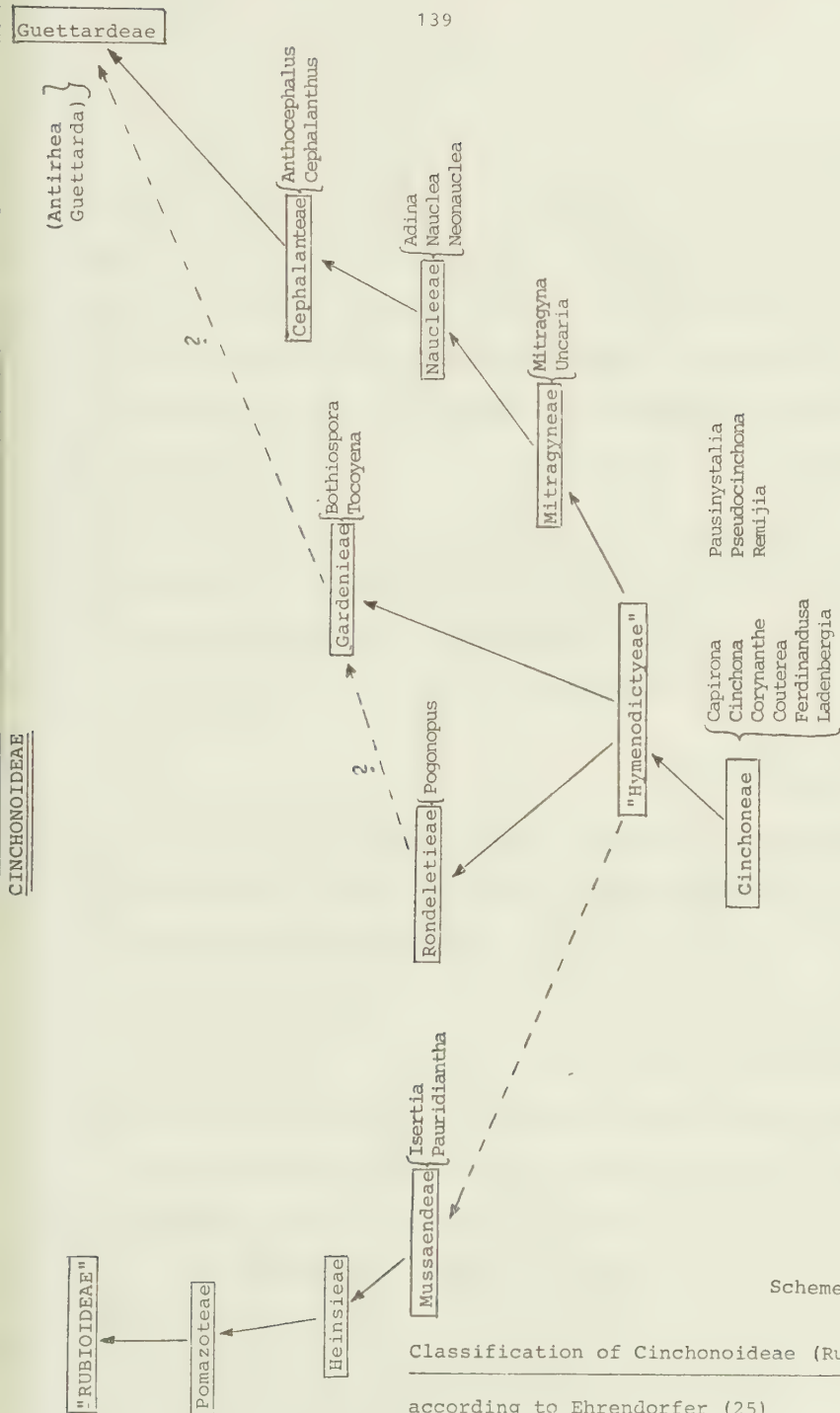
15) We are very grateful to Prof. Dr. F. Markgraf for

The botanical relationships of the tribes of the subfamily Cinchonoideae, as accepted by Ehrendorfer (25), are illustrated in scheme 16. According to the proposal of Ehrendorfer, only the species of Cinchonoideae do contain indole alkaloids with a C_9 - or C_{10} -monoterpene moiety. Compared to the classification system of Leeuwenberg (section 4.3.1), a remarkable difference seems to be worthy of mention : Ehrendorfer subdivided the Naucleae in three separate tribes, namely Mitragyneae, Naucleae and Cephalantheae. This subdivision can positively be supported by the following chemotaxonomic arguments : From the Mitragyneae species, only corynanthean (C)- and vallesiachotaman (V)-alkaloids have been isolated. Both of the genera of Mitragyneae, namely Mitragyna and Uncaria, are clearly characterized by the exclusive occurrence of oxindole alkaloids of the type C5b. Naucleae contain also alkaloids of vincosan (D)-type in addition to the corynanthean (C)- and vallesiachotaman (V)-alkaloids. In this respect, the distinction of Naucleae from Mitragyneae by Ehrendorfer can be corroborated by

18. Cont'd

his interest, constructive and valuable suggestions about the botanical classifications of the plant families discussed in this study and to Prof. F. Ehrendorfer, Vienna, for discussions.

CINCHONOIDEAE



Scheme 16.

Classification of Cinchonoideae (Rubiaceae)

according to Ehrendorfer (25)

the detection of vincosan (D)-alkaloids and the absence of the oxindol alkaloids seem to be characteristic for Mitragyneae. In Cephalanteae, alkaloids of corynanthean (C)- and vincosan (D)-types have been detected (C3 and C4d in *Cephalanthus* and D4a, D4b and D5a in *Anthocephalus*). Alkaloids of the types D4b and D5a have been isolated only from this tribe.

The outset of Rubiaceae in Cinchoneae and their ramification to the Guettardeae on the one hand, and to the Mussand^edeae on the other hand can be completely confirmed from the chemotaxonomic point of view (see later).

4.4. Loganiaceae

Loganiaceae, in contrast of Apocynaceae and Rubiaceae, have not been divided in subfamilies. Only two of the tribes, namely Gelsemineae and Strychneae, contain indole alkaloids with C₉- or C₁₀-monoterpene moiety. Only corynanthean (C)-alkaloids have been isolated from *Gelsemium* and *Mostuea* of Gelsemieae. However, the very limited number of isolations (only 4) does not allow further chemotaxonomic arguments. Of the other tribe Strychneae, *Gardneria* species contain only corynanthean (C)-alkaloids, whereas alkaloids of C-, D-, V-, S- and A-types have been isolated from the species of *Stychnos*. A peculiarity of the strychnan skeleton types lies in the fact that they contain two additional carbon atoms as skeleton members (scheme 8).

The most abundant alkaloids in Loganiaceae are of S-type (11 skeleton variations and 356 isolations). Beside the basic skeleton type S4 (e.g. akuammicine) (scheme 8), C(17) is the starting center for two additional cyclisation possibilities yielding ether rings : $C(17) + C(18)-OH \rightarrow$ S5b (e.g. diaboline) and $C(17) + C(19)-OH \rightarrow$ S5e (e.g. spermostrychnine). Additionally, two further C-atoms can be inserted between N(a) and C(16) (e.g. S6a, strychnine)). Most of these skeletons show additional variations by which C(3) is oxidized [e.g. S4 $\rightarrow$ S5d (e.g. strychnosilidine), S5e $\rightarrow$ S6b (e.g. strychnobrasiline), S6a $\rightarrow$ S7 (e.g. icajine)].

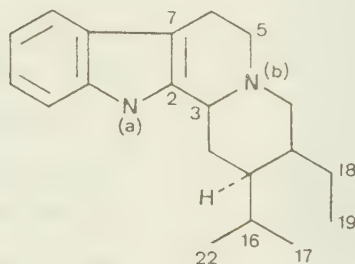
Within Strychneae, the genera Gardenia (only corynanthean (C)-alkaloids) and Strychnos can clearly be differentiated with respect to their alkaloidal content. Recently, Strychnos has been investigated chemotaxonomically (26, 27).

As already mentioned the alkaloids of corynanthean type do occur in all of the three plant families. Corresponding to scheme 4 this type can be subdivided into a vast number of skeleton variations. It also results from the same scheme that there are some obviously preferred skeleton types for certain plant families. Therefore it becomes to be inevitable to examine these types more pre-

cisely. The summary of the results is given in scheme 17. Originating with the corynanthean main type C3a and attributing the essential skeleton variations to the oxidations on the centers 2,3 and 7, and respectively to the linkage of the center C(16) with $N_{(a)}$, C(5) and C(7) and respectively of C(17) with $N_{(a)}$, $N_{(b)}$, C(7), C(18) and C(19)-O, a very interesting picture emerges : all of the C-skeleton types, which occur in Rubiaceae do contain additional bonds starting from C(17). Alkaloids which present a skeleton variation with an additional bond starting at C(16) in C3a, so far, have not been detected in Rubiaceae. The other extreme is represented by the tribe Tabernaemontaneae of Apocynaceae in which only a few C(16)-, but almost exclusively C(17)-variations of C3a could be identified. The other families, respectively tribes are placed between these two extremes. Also with respect to the oxidation state of the centers 2, 3 and 7 similar differentiations can be established : the tribe Naucleaeae of Rubiaceae produce most of the alkaloids which are oxidized at C(2). In Rauvolfieae (Apocynaceae) only 6% of all of the alkaloids are oxidized at the mentioned C-atoms.

The values given in scheme 6 allow us the following comments : Rubiaceae are clearly differentiated from Loganiaceae and Apocynaceae by the exclusive occurrence of C3a-

Scheme 17. *APOCYNACEAE*, *LOGANIACEAE*, *RUBIACEAE* - the skeleton type C3a and its reactive centers for further derivations to the more complex C-skeletons



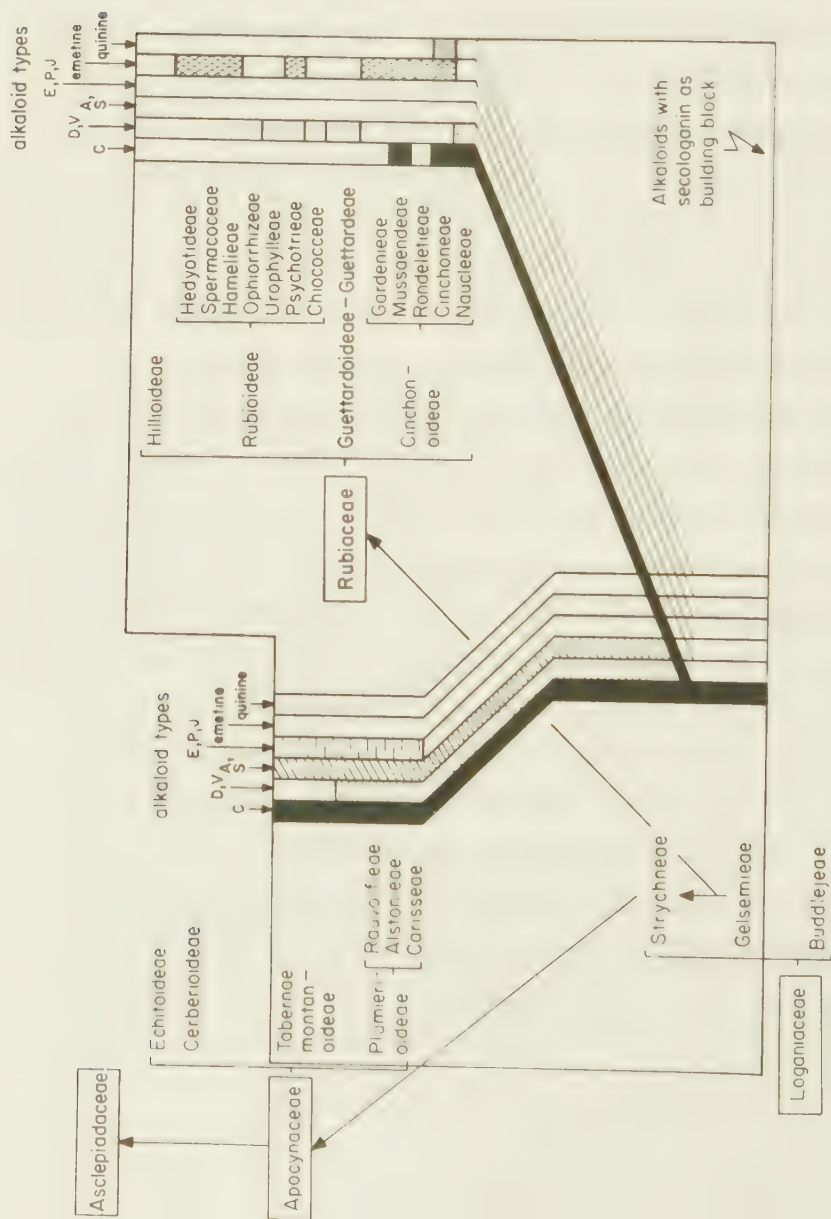
	Isolation of C-types	Oxidation at			New bonds from C(16) to				New bonds from C(17) to						Tribes %		Families %		% oxid. al- kaloids
		C(2)	C(3)	C(7)	N (a)	C(5)	C(7)	tot	N (a)	N (b)	C(18)	O-C(19)	C(7)	tot	C(16)	C(17)	C(16)	C(17)	
<i>APOCYNACEAE</i>	1089	86	179	5	36	425	94	555	-	-	199	264	132	595			48	52	25
<i>CARISSEAE</i>	64	2	4	-	8	16	25	49	-	-	3	4	1	8	86	14			9
<i>TABERNAEMONTANEAE</i>	199	10	147	-	-	188	1	189	-	-	4	4	7	15	93	7			79
<i>ALSTONIEAE</i>	326	55	19	2	27	99	55	181	-	-	46	69	37	152	54	46			23
<i>RAUVOLFIEAE</i>	599	19	9	3	1	122	13	136	-	-	146	187	87	420	24	76			6
<i>LOGANIACEAE</i>	104	13	-	6	19	38	-	57	12	-	6	5	-	23			71	29	18
<i>RUBIACEAE</i>	608	437		3	-	-	-	0	-	10	28	346	-	381			-	100	72
<i>NAUCLEEAE</i>	562	435	-	3	-	-	-	0	-	-	9	337	-	346	-	100			78
<i>CINCHONEAE</i>	43	2	-	-	-	-	-	0	-	8	19	8	-	35	-	100			5

derivatives with additional bonds starting from C(17). Within this family, Naucleaeae can also be separated from Cinchoneae by the fact, that 78% of Cinchoneae-alkaloids are oxidized at C(2) whereas only 5% of Naucleaeae-alkaloids have been detected in an oxidized state at this specific center. Further, the occurrence of alkaloids with a C(17)-N_(b)-bond in Cinchoneae is also worth mentioning. Considering this peculiar feature Cinchoneae should rather be associated with Loganiaceae. It also follows from these examinations that the formation of alkaloids of quinine type can be connected with the ability of plants to oxidize the skeleton at C(2).

The subfamily Plumerioideae of Apocynaceae which - as mentioned previously - synthesize alkaloids with rearranged secologanin show a further differentiation : with respect to the C3a-skeleton variations with additional bonds starting from C(17) Rauvolfieae are placed next to the Rubiaceae. They, however, have also a slight ability to oxidize the C-atoms 2, 3 and 7. In this respect, it is a further remarkable fact that alkaloids with other skeleton types (D, V, S, A, E, P) isolated from Rauvolfieae also do not contain additional oxidized carbon atoms facing secologanin. Tabernaemontaneae containing alkaloids very often oxidized at C(3) are clearly different from Rauvolfieae. Within other alkaloid types isolated from Tabernaemontaneae

montaneae - especially those with P- and J-skeleton - oxidized forms can also be found frequently. With C(16) as the starting center for C3a-skeleton variations, the specific character of this tribe can be emphasized once more. Though Carisseae show a similar preference for skeleton variations at C(16) as Tabernaemontaneae, they do not have a strong tendency to oxidize the mentioned C-atoms (this fact can be noticed also by the alkaloids of other skeleton types). Alstonieae in which a remarkable tendency towards the oxidation at C(2)* can be observed should be located between Carisseae and Rauvolfieae. The plumeran alkaloids occurring in Alstonieae frequently have an additional oxygen substituent at C(21).

Not only concerning the common occurrence of different skeleton types, but also of the variations of C-skeleton, Loganiaceae give evidence for their essential role : it can easily be inferred that Loganiaceae are placed closer to Apocynaceae than to Rubiaceae. Further, Carisseae should be directly joined up with Loganiaceae. Then, Tabernaemontaneae, Alstonieae and finally Rauvolfieae follow. On the other side Rubiaceae are placed being connected over Cinchoneae according to the classification of Ehrensdoerfer. This statement proceeds from scheme 18.



An attempt to differentiate the genera more precisely, with respect to the occurrence of the alkaloids, has been successful only to a certain extent (some examples have already been mentioned), because, besides the genera investigated intensively (e.g. *Catharanthus*, *Rauvolfia*, *Uncaria*) there are also some genera which have not been examined closely. There are species from which many alkaloids have been isolated, on the other hand there are also species in which so far, only one alkaloid could be detected. Hitherto, it has not been possible to set a quantitative criterion to say, that only one alkaloid but no other can be isolated. However, it still seems plausible to find chemotaxonomic considerations, if there are available quantitative examinations of the plant in question (these considerations should regard the seasons, the native region and the part of the plant under examination).

Table 28¹⁶. Catalogue of the indole alkaloids with
C₉- or C₁₀-monoterpene moiety occurring
in the plant families APOCYNACEAE,
LOGANIACEAE and RUBIACEAE.

-
- 16) In this table the families, genera, species and skeleton types (A, C, D, V, ...) are listed alphabetically. The tribes to which the listed genera belong are indicated with corresponding abbreviations in parentheses. Both skeleton types are given for the bisindole alkaloids (e.g. C4f - C5e : (+)-villalstonine). If known, the absolute configuration of the isolated alkaloids are also illustrated as α , β , as mentioned in scheme 2. The following symbols were used : (+)-alkaloid (α) : the alkaloid has the absolute configuration α , $[\alpha]_D = +$; (+)-alkaloid ($\alpha + \beta$) : racemate; (O)-alkaloid (α) : the specific rotation is 0, but it is not a racemate; ()-alkaloid (β) : the absolute configurations is known, but not the specific rotation; alkaloid* : C(15) is not a center of chirality. - We have attempted to cite all the references up to the end of 1978. By plumeran alkaloids, only those isolations are listed which were either not considered in ref.2 or have been isolated since than.

APOCYNACEAE (APO)Alstonia (ALS)

A. actinophylla (Cunn) K. Schum. (= *A. verticillosa* F.v.Müll.): C5g : (-)-echitamine (α ; 5a). - *A. angustiloba* Miq. : C5g : (-)-echitamine (α ; 28). - *A. boonei* De Wild. : C4c : akuammidine (29); C5g : echitamine (30); J7a : voacangine (29). - *A. congensis* Engl. (= *A. gillettii* De Wild.) : C5g : (-)-echitamine (α ; 28); S4 : (-)-echitamidine (α ; 31). - *A. constricta* F.v.Müll. : C4a : (+)-alstonine (α ; 32, 33), tetrahydro-alstonine (33); C4b : alstoniline* (34), (-)-reserpine (α ; 35), α -yohimbine (33); C5c : (-)-O-3,4,5-trimethoxy-benzoyl-vincamajine (α ; 36), (-)-O-3,4,5-trimethoxy-cinnamoyl-vincamajine (α ; 36), (-)-vincamajine (α ; 36), C5r : alstonilidine* (36); C5s : (-)-alstonidine (36). - *A. deplanchei* van Heurck et Müll. Arg. : C4e : cabucraline (37); C4e - C4f : (+)-pleiocraline (38); C4f - C5g : (+)-pleiocorine (39); C5g : vincorine (37). - *A. gillettii* De Wild. (see *A. congensis*). - *A. glabriflora* Mgf. : C4f: (+)-pleiocarpamine (α ; 40); C4f - C5e : (+)-villalstonine (40); C5e : (-)-alstophylline (40); C5e - C5e : (+)-macralstonine (40). - *A. lanceolifera* S. Moore (see *A. lenormandi* var. *lanceolifera*). - *A. lenormandi* von Heurck et Müll. Arg. var. *lanceolifera* (S. Moore) Monach.) (= *A. lanceolifera* S. Moore) :

C4c : (+)-N_(a)-methyl-10-methoxy-akuammidine (41),
 N_(b)-methyl-10-methoxy-akuammidine (42); C5c : (-)-10-
 methoxy-vincamajine (α; 41), (-)-O-3,4,5-trimethoxy-
 benzoyl-hydroxy-vincamajine (α; 41), (-)-O-3,4,5-
 trimethoxycinnamoyl-vincamajine (α, 41), (-)-O-3,4,5-
 trimethoxycinnamoyl-10-methoxy-vincamajine (α; 41),
 (-)-O-3,4,5-trimethoxycinnamoyl-10-hydroxy-vincamajine
 (α; 41); C6d : (-)-10-hydroxy-lanciferine (α; 42),
 (-)-lanciferine (α; 42), (-)-10-methoxy-lanciferine
 (α; 42). - *A. macrophylla* Wall. : C4c : (+)-affinisine
 (α; 43); C4c - C5e : (+)-macralstonidine (44); C4f :
 (+)-pleiocarpamine (α; 44); C4f - C5e : (-)-macro-
 carpamine (45), (+)-villalstonine (46); C5c : (-)-O-
 benzoyl-vincamajine (α; 47), quebrachidine (48); C5d :
 (-)-picralstonine (43), (-)-picrinine (α; 43); C5e :
 (-)-alstophylline (49); C5e - C5e : (+)-macralstonine
 (50); D6c : (+)-macrosalhinine (51); S4 : N_(a)-methyl-
 2,16-dihydro-akuammicine (44). - *A. muelleriana* Domin :
C4f : 2,7-dihydro-pleiocarpamine (52), pleiocarpamine
 (52); C4f - C5e : (+)-villalstonine (52,53); C5c : que-
 brachidine (52); C5c - C5e : (-)-alstonisidine (52,54);
C5e : (-)-alstonerine (52, 55); C5e - C5e : (+)-macralsto-
 nine (52, 57), (+)-N'_(a)-demethyl-anhydromacralstonine
 (52); C6e : (+)-alstonisine (52,55); S4 : 11-methoxy-

akuammicine (58), (-)-vinervinine (52). - *A. nerifolia*
 G. Don.: C5g : echitamine (59). - *A. quaternata* van
 Heurck et Müll. Arg. : A4a : (+)-tubotaiwine (α ; 60);
C4b : (+)-pseudoyohimbine (α ; 60), (+)-quaternatine
 (α ; 60), (+)-yohimbine (α ; 60); C4e : ()-cathafoline
 (α ; 60), (-)-quaternoxine (60); C5c : (-)-vincamajine
 (α ; 60); C5d : (-)-quaternidine (60), (-)-quaternine
 (α ; 60); C5u : quaternoline (60). - *A. scholaris* (L.)
 R. Br. : A4a : tubotaiwine (61, 62); C4a : tetrahydro-
 alstonine (63); C4c : akuammidine (64, 65); C4e :
 strictamine (63); C5d : (-)-picralinal (α ; 64); (-)-
 picrinine (α ; 61,64); C5g : (-)-echitamine (α ; 59,61,62),
 norechitamine (61, 62); C5h : pseudoakuammigine (61, 62),
C5v : (-)-nareline (α ; 66); S4 : akuammicine (61, 62),
 akuammicine-methiodide (61, 62), akuammicine-N-oxide
 (61, 62), (-)-echitamidine (α ; 31,62); 18- or 19-hydroxy-
 19,20-dihydro-akuammicine (61), hydroxy-19,20-dihydro-
 akuammicine (61, 62). - *A. somersetensis* Bailey (see
A. spectabilis). - *A. spatulata* Bl. : C5g : (-)-echitamine
 (α ;). - *A. spectabilis* R. Br. (= *A. somersetensis*
 Bailey, *A. villosa* Blume) : C4c : (+)-N_(a)-methyl-
 sarpagine (α ; 40); C4c - C5e : (+)-macralstonidine (40);
C4f : (+)-pleiocarpamine (α ; 40); C4f - C5e : (+)-
 villalstonine (40, 67); C5c : (+)-quebrachidine (α ; 40),

(-)-vincamajine (α ; 40); C5g : echitamine (68). -
A. venenata R. Br. : C4b : 3,4-dehydro-alstovenine
 (69), anhydro-alstonatine* (70), (+)-isovenenatine
 (α ; 71), reserpine (71), (-)-venenatine (α ; 71),
 (-)-veneserpine (α ; 72), (-)-venoxidine (α ; 73). -
A. villosa Blume (see *A. spectabilis* R. Br.). -
A. vitiensis (Seem.) var. *novo ebudica* Monach. :
C4e : (-)-cabucraline (α ; 37), quaternoxine (37);
C4f : pleiocarpamine (37); C5g : (-)-vincorine (α ;
 37); S4 : (-)-alstovine (37).

Ammocallis (ALS)

A. rosea Small (see *Catharanthus roseus*).

Amsonia (ALS)

A. angustifolia (Ait.) Michx. (see *A. ciliata*). - *A.*
ciliata Walt. (= *A. angustifolia* (Ait.) Michx.) : C3a :
 angusteine (74); C4b : β -yohimbine (5b); C4c :
 akuammidine (74); E5a : (-)-eburnamenine (α ; 74), (+)-
 eburnamonine (β ; 74); P5 : (+)-vincadiformine (β ; 74);
S4 : angustimycine (74); V4 : angustine* (74). - *A.*
elliptica (Thunb.) R. et Sch. : C3a : 10-hydroxy-
 geissoschizol (75, 76); C4a : tetrahydroalstonine (75, 77);
C4b : 3,4,5,6-tetrahydro- β -yohimbinium-chloride (75, 76),
 (+)-yohimbine (α ; 75, 76), (-)- β -yohimbine (α ; 75, 76);
C4f : (+)-pleiocarpamine (α ; 75, 76); E5a : 14,15-dehydro-

vincamine (75, 77), 16-epi-14,15-dehydro-vincamine (75, 77); P3 - P3 : presecamine (75), secamine (75), tetrahydro-presecamine (75); P5 : 16-carbomethoxy-16-hydroxy-14,15-epoxy-3-oxo-1,2-dehydro-aspidospermidine (77), 14,15-epoxy-3-oxo-vincadifformine (75, 77), (-)-3-oxo-tabersonine (75, 77), (-)-tabersonine (α ; 75, 77), tabersonine-N-oxide (77); V3 : (+)-antirrhine (α ; 75, 76), antirrhine- α -methochloride (75, 76). - *A. tabernaemontana* Walt. : A4a : (+)-19,20-dihydro-condylocarpine (α ; 78); C3a : (-)-18,19-dihydro-corynantheol (α ; 78); C4a : (-)-tetrahydroalstonine (α ; 78, 79); C4c : (+)-akuammidine (α ; 78); E5a : (-)-eburnamine (β ; 79, 80), (+)-eburnamonine (β ; 79), isoeburnamine (80); S4 : (-)-nor-fluorocurarine (α ; 79).

Anacampta (TAB)

A. rigida (Miers) Mgf. (= *Phrissoecarpus rigidus* Miers, *Tabernaemontana macrophylla* Miers; *T. rigida* Miers) : E5a : (+)-apovincamine (α ; 81), (-)-16-epi-vincamine (α ; 81), (+)-16-epi-vincamine (α + β ; 81), (+)-vincamine (α ; 81), (+)-vincamine (α + β ; 81). - *A. rupicola* (Benth.) Mgf. (= *Tabernaemontana rupicola* Benth.) : J8a : (-)-rupicoline (82), (-)-voacristine-pseudoindoxyl (β ; 82).

Aspidosperma (ALS)

A. album (Vahl.) R. Bent. : A4a : (+)-condylocarpine (α ; 83), (+)-tubotaiwine (α ; 83); A5b : (+)-andranginine ($\alpha + \beta$; 83); C3a : (+)-16-epi-sitsirikine (α ; 83), (-)-isositsirikine (α ; 83), (+)-sitsirikine (α ; 83); E5a : (+)-vincamine ($\alpha + \beta$; 83); P5 : (-)-N-acetyl-aspidospermidine (α ; 83), (+)-aspidospermidine (83), (+)-limaspermine (β ; 83), (+)-11-methoxy-limaspermine (β ; 83), (+)-vincadifformine (β ; 83); P6d : (+)-fendlerine (β ; 83); P7e : (-)-alalakine (83). - *A. auriculatum* Mgfl. : C3a : (-)-dihydro-corynantheol (α ; 84); C4a : reserpiline (84). - *A. carapanauba* Pichon : C5b : (-)-carapanaubine (α ; 85). - *A. compactinervum* Kuhlmann (see *A. eburneum*). - *A. cuspa* (H.B.K.) Blake : C3a : (-)-16-epi-sitsirikine (α ; 86); C5d : (-)-desacetyl-picraline (α ; 87); C6d : (-)-aspidodasycarpine (α ; 86, 87); P7a : (-)-22-epi-kopsanol (α ; 86), kopsanol (86), (-)-kopsanone (α ; 86). - *A. dasycarpon* A. DC. (see *A. tomentosum*). - *A. desmanthum* Benth. ex Müll. Arg. : P6d : aspidobalbine (88). - *A. discolor* A. DC. : C3a : (-)-10-methoxy-dihydro-corynantheol (α ; 89), (-)-10-methoxy-geissoschizol (α ; 89); C4a : (-)-isoreserpiline (α ; 89), (-)-reserpiline (α ; 89); C4b : (+)-yohimbine (α ; 89), (-)- β -yohimbine (α ; 89); C5m : (-)-isoreserpiline-

pseudoindoxyl (α ; 89). - *A. eburneum* F. Allem (= *A. compactinervum* Kuhlmann) : A4a : N-acetyl-11-hydroxy-aspidospermatidine (84); C4b : (-)- β -yohimbine (α ; 90); S4 : (-)-compactinervine (α ; 91). - *A. exalatum* Monach. : P5 : N-acetyl-aspidospermidine (92), aspidospermine (92), demethoxy-palosine (92), O-demethyl-palosine (92), limaspermine (92); P6d : cimicine (92), fendlerine (92). - *A. excelsum* Benth. : C3a : (-)-aspexcine (5b), methoxy-geissoschizoline (5b); C4b : ()-O-acetyl-yohimbine (α ; 93), (-)-excelsinine (α ; 93), (+)-yohimbine (α ; 93), (-)- α -yohimbine (α ; 94). - *A. formosanum* A.P. Duarte : P5 : (+)-aspidocarpine (β ; 88). - *A. laxiflorum* Kuhl. (see *A. rigidum*). - *A. limae* Woods. : A4a : (+)-limatine (α ; 95), (+)-limatinine (α ; 95), (+)-11-methoxy-limatine (α ; 95), (+)-11-methoxy-limatinine (α ; 95), (+)-tubotaiwine (α ; 95). - *A. marcgravianum* Woods. : C3a : (-)-dihydro-corynantheol (α ; 96); C4a : aricine (97), reserpiline (97). - *A. neblinae* Monach. : E5a : eburnamonine (98). - *A. nitidum* Benth. ex Müll. Arg. : C3a : (-)-10-methoxy-dihydro-corynantheol (α ; 97). - *A. oblongum* A. DC. : C3a : alkaloid II/296 (99), alkaloid II/298 (99), alkaloid II/328 (99), alkaloid III/352 (99), alkaloid III/354 (99), alkaloid

III/382 (99), alkaloid III/384 (99), alkaloid IV/354 (99), alkaloid IV/356 (99), alkaloid IV/384 (99), alkaloid IV/386 (99), (-)-10-methoxy-geissoschizol (α ; 84); C4a : alkaloid I/352 (99), alkaloid I/382a (99), alkaloid I/382b (99), isoreserpiline (99), reserpiline (99); C4b : 11-methoxy-yohimbine (100), (+)-pseudoyohimbine (α ;101), yohimbine (101), (-)- β -yohimbine (α ;100). - *A. peroba* F. Allem ex Sald. (see *A. polyneuron*). - *A. polyneuron* Müll. Arg. (= *A. peroba* F. Allem. ex Sald.) : A4a : aspidospermatine (102); C4b : yohimbine (102); C4c : (+)-macusine B (α ;103), (+)-normacusine B (α ; 90), (-)-polyneuridine (α ; 90). - *A. populifolium* A. DC. : A4a : (+)-11-methoxy-19,20-dihydro-condylocarpine (84). - *A. pyricollum* Müll. Arg. : A3 : (+)-stemmadenine (α ;97); C4b: (+)-19,20-dehydro-yohimbine (α ;104), yohimbine (104), β -yohimbine (104). - *A. quebracho-blanc* Schlecht. : A4a : N_(a)-acetyl-aspidospermatidine (105), aspidospermatidine (105), (-)-aspidospermatine (α ;105), desacetyl-aspidospermatine (105), 19,20-dihydro-aspidospermatine (105), N_(a)-methyl-aspidospermatidine (105); C4b : yohimbine (105); C4c : akuammidine (106); C5c : (+)-quebrachidine (α ;107); E5a : eburnamenine (108). - *A. rigidum* Rusby (= *A. laxiflorum* Kuhl.). : C4a : reserpiline (97); C5b : (-)-carapanaubine (α ; 97); C5d : desacetyl-picraline (97), picraline (97). -

A. spegazzini Molf (see *Rauvolfia schuelii*). - *A. species* No. 9610 : A4a : (+)-11,12-dihydroxy-N-acetyl-aspidospermatidine (109). - *A. species* No. RJB 119070 : C3a : 10-methoxy-dihydro-corynantheol (84). - *A. tomentosum* Mart. (= *A. dasycarpon* A. DC.) : A4a : (+)-limatinine (α ; 97); C4c : polyneuridine (110); C6d : (-)-aspidodasycarpine (α ;110).

Bleekeria (RAU)

B. coccinea (Miq.) Koidz. (see *Ochrosia coccinea*). -
B. compta (K. Schum.) Wilbur. (see *Ochrosia compta*). -
B. elliptica (Labill.) Koidz. (see *Ochrosia elliptica*). -
B. vitiensis (Mgf.) A.C. Smith (see *Ochrosia vitiensis*). -

Bonafousia (TAB)

B. killipii (Woods.) Mgf. (= *Tabernaemontana killipii* Woods., *B. tetrastachya* (Humboldt, Bompland et Kunth) Mgf.) : C3a : (+)-geissoschizine (α ;111); J7a : (-)-bonafousine (β ;112), (-)-coronaridine (β ;113), (-)-isovoacangine (β ;113), (-)-voacangine (β ;113); J7a - J7a : (-)-bis-(11-hydroxy-coronaridinyl-12) (β - β ;113). - *B. tetrastachya* (Humboldt, Bompland et Kunth) Mgf. (see *B. killipii*).

Cabucala (RAU)

C. erythrocarpa var. *erythrocarpa* (Vatke) Mgf. : C4a : (-)-aricine (α ; 18), (-)-cabucine (α ; 18), (O)-cabucinine (α ; 18); C4b : reserpine (18); C4c : (+)-vellosimine (α ; 18); C4e : (-)-cabucraline (α ; 18); C5a : (-)-ochropamine (18); C5c : (+)-quebrachidine (α ; 18,19); C5g : (-)-cabuamine (α ; 18,114), (-)-deformo-cabuamine (α ; 18), vincorine (37); C5h : (-)-akuammine (α ; 18); S4 : (-)-akuammicine (α ; 18). - *C. fasciculata* Pichon : C4a : (-)-cabucine (α ; 115), (O)-cabucinine (α ; 115); C5b : (-)-caboxine A (α ; 115,116), (-)-carapanaubine (α ; 115), (+)-10,11-dimethoxy-isomitraphylline (115), (+)-isocaboxine A (α ; 115,116), (+)-isocaboxine B (α ; 115,116), (+)-rauvoxine (α ; 115); C5h : (-)-O-methyl-akuammine (α ; 115). - *C. glauca* Pichon (see *C. madagascariensis*). - *C. madagascariensis* (A. DC.) Pichon (= *C. glauca* Pichon) : C4a : (-)-cabucine (α ; 117), (O)-cabucinine (α ; 117); C4b : (-)-reserpine (α ; 117). - *C. striolata* Pichon : C4a : (-)-ajmalicine (α ; 118), (O)-ajmalicinine (α ; 118), (-)-cabucine (α ; 118), (O)-cabucinine (α ; 118), (-)-10,11-dimethoxy-ajmalicine (α ; 118), (-)-10,11-dimethoxy-ajmalicinine (α ; 118); C4b : (-)-reserpine (α ; 118); C5c : (+)-quebrachidine (α ; 118). - *C. torulosa* Pichon : C4a : (-)-aricine (α ; 119),

(-)-cabucine (α ;119), (-)-tetrahydro-alstonine (α ;119);

C4e : (-)-cabucraline (α ;119); C5c : (+)-quebrachidine (α ;119), (-)-vincamajine (α ;119).

Callichilia (TAB)

C. barteri (Hook. F.) Stapf (see *Hedranthera barteri*). -

C. subsessilis Stapf : P6e - P6e : (-)-amataine (α - α ;120).

Capuronetta (TAB)

C. elegans Mgf. : C5a - J8b : (-)-capuvosine (α - β ;121), (-)-dehydroxy-capuvosine (122), (-)-N-demethyl-capuvosine (122); C5a - J9a : (-)-capuvosidine (α - β ;122); J8b : (+)-capuronine (β ;121); J9a : (-)-14,15-anhydro-capuronidine (β ;122), (-)-14,15-anhydro-1,2-dihydro-capuronidine (β ;122), (+)-capuronidine (β ;121).

Carpodinus (CAR)

C. umbellatus K. Schum. (see *Hunteria umbellata*).

Catharanthus (ALS)

C. lanceus (Boj. ex A.DC.) Pichon (= *Vinca lancea* (ex A. DC.) K. Schum.; *Lochnera lancea* Boj.) : C4a : (-)-ajmalicine (α ;123), (-)-tetrahydro-alstonine (α ;123); C4b : (+)-yohimbine (α ;123); C4c : (+)-peri-

cyclivine (α ;124); C5a : ()-periformyline (α ;125),
 ()-perivine (α ;126); P5 : (-)-14,15-dehydro-19-epi-
 minovincinine (α ;127); J7a : catharanthine (128); J8b - P5 :
 (+)-leurosine (α - α ;129); J9b - P5 : (-)-catharine (α - α ;130). -
C. longifolius Pichon : C4a : ajmalicine (131); C4c :
 akuammidine (131), normacusine B (131), pericyclivine
 (131); C4e : (-)- cabucraline (α ; 37); C5a : perivine (131);
J7a : ()-catharanthine (α ;131); J8b - P5 : ()-leurosine
 (α - α ;131), vinblastine (131); J9b - P5 : catharine (131);
J9c - P5 : (-)-catharinine (α - α ;132); P5 : desacetyl-
 vindoline (133); P6a : 15-hydroxy-kopsinine (133); P6c :
 cathovaline (133); S4 : akuammicine (131), 2,16-dihydro-akuammicine
 (131), N_(a)-methyl-2,16-dihydro-akuammicine (131); V3 : antirhine (131). -

C. ovalis Mgf. : C4a : (+)-serpentine (α ;134); J7a :
 (+)-catharanthine (α ;134), (-)-coronaridine (β ;134);
J8b - P5 : vincovalicine (135), (-)-vincovaline (β - α ;135),
 vincovalinine (135); J9b - P5 : (-)-catharine (α - α ;136);
J9c - P5 : (-)-catharinine (α - α ;132); P5 : (-)-catho-
 valinine (α ;137), ()-19-epi-19-hydroxy-tabersonine
 (α ;138), ()-19-hydroxy-tabersonine (α ;138). - *C. pusillus*
 (Murr.) G. Don. (= *Vinca pusilla* Murr.) : C4a : (-)-ajma-
 licine (α ;139); C4b : α -yohimbine (140). - *C. roseus* (L.)
 G. Don. (= *Vinca rosea* (L.) Reichb., *Ammocallis rosea* Small,
Lochnera rosea Reichb.) : A3 : stemmadenine (141); C3a :

corynantheine (141), corynantheine-aldehyde (141),
 (-)-dihydro-sitsirikine (α ;142), geissoschizine (141),
 (-)-isositsirikine (α ;142), (+)-sitsirikine (α ;83,142);
C4a : (-)-ajmalicine (α ;143), alstonine (5b), (+)-
 serpentine (α ;143), (-)-tetrahydroalstonine (α ;143); C4b :
 (-)-reserpine (α ;143); C4c : (+)-lochnerine (α ;144);
C5a : (-)-perivine (α ;145); C5b : (-)-mitraphylline
 (α ;143); C5h : (-)-akuammine (α ;143); D3a : (-)-strictosi-
 dine (α ;10), (-)-vincoside (α ;10,141); E6b: (-)-vincarodine (α ;146,147);
J7a: (+)-catharanthine (α ;145), coronaridine (141); J8b - P5 :
 (+)-desacetoxy-vinblastine (α - α ;148), (+)-isoleurosine
 (α - α ;149,150), leurocolombine (151), (+)-leurocristine
 (α - α ;152), (+)-leurosidine (α - α ;153), (+)-leurosine (α - α ;145,150),
 (+)-pleurosine (α - α ;154), pseudovincaleukoblastine-diol
 (151), (+)-vinblastine (α - α ;145); J9b - P5 : (-)-catharine
 (α - α ;136,149); J9c - P5 : catharinine (α - α ;132); J9d - P5 :
 vincathicine (155); P6a: venalstonine (156); P6f: ()-vincoline (α ;138,157);
S4: (-)-akuammicine (α ;141,143), (-)-lochneridine (α ; 91), ()-preakuammi-
 cine (α ;141). - *C. trichophyllum* (Bak.) Pichon: C4a: (-)-ajmalicine (α ;158)
 (-)-tetrahydro-alstonine (α ;158); C4b : (+)-pseudoyohimbine
 (α ;159); P5 : (-)-cathaphylline (α ;159), (-)-echitovenine
 (α ;159), (-)-hoerhammericine (α ;159), (-)-lochnericine (α ;
 159), (-)-minovincine (α ;159), (-)-minovincinine (α ;159),
 vindorosine (159); P6b : (-)-vindolinine (α ;158); S4 :
 akuammicine (159).

Conopharyngia (TAB)

C. brachyantha Stapf (= *Tabernaemontana brachyantha* Stapf) : C4c : (+)-normacusine B (α ;160); C5a - J7a : (-)-19-epi-voacordine (α - β ;160), (-)-voacordine (α - β ;160); C6c : (-)-anhydro-vobasine-diol (α ;160). - *C. contorta* (Stapf) Stapf 1904 (= *Tabernaemontana contorta* Stapf 1894) : J7a : conopharyngine (161), coronaridine (161), (-)-ibogaine (β ;161), (-)-voacangine (β ;161), voacristine (161). - *C. crassa* (Benth.) Stapf (= *Tabernaemontana crassa* Benth.) : J7a : conopharyngine (162), (-)-19-hydroxy-conopharyngine (162); J8d : (+)-crassanine (162). - *C. cuminsii* (Stapf) Stapf (= *Tabernaemontana pachysiphon* Stapf, *Tabernaemontana pachysiphon* Stapf var. *cuminsii* H. Huber) : C5a : (-)-affinine (α ;161); J7a : (-)-conopharyngine (β ;161), coronaridine (161), jollyanine (163), 19-hydroxy-conopharyngine (164), (-)-voacangine (β ;161); J8a : conopharyngine-pseudoindoxyl (164). - *C. durissima* Stapf : C4e : (+)-akuammiline (α ;165); C5a - J7a : (-)-conoduramine (α - β ;166), (-)-conodurine (α - β ;166); C6c : (-)-anhydrovobasine-diol (α ;165); J7a : (-)-conopharyngine (β ;167), (-)-coronaridine (β ;168), (-)-hydroxy-indolenine-coronaridine (β ;168), (-)-isovoacangine (β ;167). - *C. elegans* (Stapf) Stapf (= *Tabernaemontana elegans* Stapf) : C5a : (-)-dregamine (α ;169), (-)-tabernaemontanine (α ;169);

C5a - J7a : (-)-conoduramine (α - β ;169,170), (-)-tabernaelegantine A (169,170), (+)-tabernaelegantine B (169,170), (-)-tabernaelegantine C (169,170), (+)-tabernaelegantine D (169,170), (-)-tabernaelegantinine A (169,170), (+)-tabernaelegantinine B (169,170). - *C. johnstonii*

Stapf (= *Tabernaemontana johnstonii* Pichon) : A4a : (+)-tubotaiwine (α ;171), (+)-tubotaiwine-N-oxide (α ;171);

C4c : pericyclivine (172); C5a : perivine (172);

C5a - J7a : conoduramine (172), conodurine (172), 19,20-epoxy-conoduramine (172), gabunamine (172), gabunine (172), (-)-tabernamine (α - β ;172,173); J7a : ibogamine (172), isovoacangine (172). - *C. jollyana*

Stapf (= *Tabernaemontana jollyana* (Stapf) Pichon) :

C4c : O-acetyl-polyneuridine (174); J7a : (-)-coronaridine (β ;175), heyneanine (174), 19-hydroxy-conopharyngine (174), 19-hydroxy-coronaridine (174), 19-hydroxy-3-oxo-coronaridine (176), (-)-jollyanine (174), (-)-3-oxo-conopharyngine (176), 3-oxo-coronaridine (176), voacristine (174). - *C. longiflora* (Benth.)

Stapf : C5a - J7a : 18'-decarbomethoxy-voacamine (5b), voacamine (5b), voacarine (5b); J7a : conopharyngine (177), voacangine (177), voacristine (5b). - *C. pachysiphon* Stapf (see *C. cumminsii* (Stapf) Stapf). -

C. penduliflora (K. Schum.) Stapf (= *Tabernaemontana*

penduliflora K. Schum.) : J7a : (-)-conopharyngine (β ;161), coronaridine (161), voacangine (161).- *C. retusa* G. Don. (see *Pandaca retusa*).

Craspidospermum (ALS)

C. verticillatum Boj. ex A. DC. : A4a : (+)-tubotaiwine (α ;178); E5a : ()-14,15-dehydro-16-epi-vincine (α ;179,180), (+)-14,15-dehydro-vincine (α ;179,180); E6b : (-)-craspidospermine (α ;180); P5 : (-)-11-hydroxy-tabersonine (180). - *C. verticillatum* Boj. var. *petiolare* A.de Candolle : A3 : (+)-deformostemmadenine (181), stemmadenine (181); A4a : condylocarpine (181); A5b : (+)-andranginine (α + β ;17,181); E5b : (-)-andrangine (α ;181).

Crioceras (TAB)

C. dipladeniiflorus (Stapf) K. Schum. : E5a : (+)-apo-14,15-dehydro-vincamine (α ;182,183), (+)-14,15-dehydro-vincamine (α ;182,183), (+)-16-epi-14,15-dehydro-vincamine (α ;182,183), (+)-12-methoxy-14,15-dehydro-vincamine (α ;182,183,184); E5b : (-)-andrangine (α ;185); E5b - P5 : (-)-criophylline (185,186); E6b : (-)-criocerine (α ;183). - *C. longiflorus* Pierre : E5a : (+)-16-epi-14,15-dehydro-vincamine (α ;187), (+)-14,15-

dehydro-vincamine (α ;187); P6e - P6e : (-)-vobtusine (α - α ;187).

Diplorrhynchus (ALS)

D. condylocarpon (Müll. Arg.) Pichon subsp. *mossambicensis* (Benth.) Duvign.: A3 : (+)-stemmadenine (α ;188,189); A4a : (+)-condylocarpine (α ;198); C4b : (+)-yohimbine (α ;189), (-)- β -yohimbine (α ;189); C4c : (+)-normacusine B (α ;189); S4 : (-)-mossambine (α ;189), (-)-norfluorocurarine (α ;189).

Ervatamia (TAB)

E. coronaria (Jacq.) Stapf (= *Tabernaemontana coronaria* R. Br.) : C5a : dregamine (190,191), (-)-tabernaemontanine (α ;190,191); J7a : (-)-coronaridine (β ;190,192), (-)-3-oxo-coronaridine (β ;192), voacangine (193), voacristine (190). - *E. dichotoma* (Roxb.) Blatter : J7a : coronaridine (194), (-)-heyneanine (β ;195), (-)-hydroxy-indolenine-voacristine (β ;195). - *E. divaricata* (L.) Burk. (= *Tabernaemontana divaricata* R. Br. ex Roem. et Schult.) : C5a : (-)-tabernaemontanine (α ;196); J7a : (-)-coronaridine (β ;196), (-)-voacangine (β ;196); P4 : (+)-conoflorine (196); P5 : (-)-lochnericine (α ;196). -

E. macrocarpa Merr. (see *Pagiantha macrocarpa*). - *E. mucronata* Merr. (Mgf.) (= *Tabernaemontana mucronata* Merr.) : C5a : tabernaemontanine (197); J7a : coronaridine (197). - *E. obtusiuscula* Mgf. : J9a : ()-20-epi-pandoline (β ;198), ()-pandoline (β ;198). - *E. orientalis* (R. Br.) Domin (= *Tabernaemontana orientalis* R. Br.) : C5a : (-)-dregamine (α ;199), (-)-tabernaemontanine (α ;199), vobasine (199); C5a - J7a : (+)-16-decarbomethoxy-dihydro-voacamine (α - β ;199), (+)-16-decarbomethoxy-20'-epi-dihydro-voacamine (α - β ;199), decarbomethoxy-voacamine (199), voacamine (199); C7b : (+)-19-dehydro-ervatamine (α ;199), (-)-20-epi-ervatamine (α ;199), (-)-ervatamine (α ;199); J7a : (-)-ibogaine (β ;199), (-)-iboxygaine (β ;199), (-)-voacristine (β ;199). - *E. pandacaqui* (Poir.) Pichon (= *Tabernaemontana pandacaqui* Poir.) : C4c : deformato-akuammidine (200); C5a : (-)-tabernaemontanine (α ;200); J7a : (-)-coronaridine (β ;201); J10d - P5 : (+)-ervafolidine (α - β ;200), (+)-ervafoline (α - β ;200), (+)-isoervafolidine (α - β ;200); S4 : (+)-20-epi-lochneridine (β ;200).

Excavatia (RAU)

E. balansae Guill. (see *Ochrosia balansae*). - *E. coccinea* (Teysm. et Binn.) Mgf. (see *Ochrosia coccinea*). - *E. elliptica* (Labill.) Mgf. (see *Ochrosia elliptica*). - *E. vitiensis* Mgf. (see *Ochrosia vitiensis*).

Gabunia (TAB)

G. eglandulosa (Stapf) Stapf (= *G. longiflora* Stapf, *Tabernaemontana chartacea* Pichon, *T. eglandulosa* (Stapf) Pichon) : C5a : perivine (202), vobasine (202); C5a - J7a : voacamine (202); J7a : conopharyngine (161), (-)-coronaridine (β ;161,202), (-)-eglandulosine (β ;203), 19-hydroxy-coronaridine (202), (-)-3-hydroxy-isovoacangine (β ;202), (-)-isovoacangine (β ;202), (-)-voacangine (β ;161); J8c : (-)-eglandine (β ;203). - *G. longiflora* Stapf (see *G. eglandulosa*). - *G. odoratissima* Stapf (= *Tabernaemontana odoratissima* (Stapf) Pichon) : C4c : (+)-pericyclivine (α ;204); C5c : (-)-perivine (α ;204), (-)-vobasine (α ;204); C5a - J7a : (-)-conoduramine (α - β ;204), (-)-conodurine (α - β ;204), (-)-gabunine (α - β ;204); J7a : (-)-coronaridine (β ;204), (-)-ibogamine (β ;204), (-)-isovoacangine (β ;204).

Geissospermum (ALS)

G. argenteum Wood. : P5 : (+)-aspidocarpine (β ;205), (-)-aspidospermine (β ;205), (-)-demethoxy-aspidospermine (α ;205), (+)-demethyl-aspidospermine (205). - *G. laeve* (Vell.) Baill. (see *G. vellosii*). - *G. sericeum* (Sagot) Benth. et Hook. : C3a - S5a : (-)-geissospermine (α - α ;206). - *G. vellosii* F. Allem. (= *G. laeve* (Vell.) Baill., *Tabernaemontana laevis* Vell.) : A5a : (-)-geissovelline (207);

C3a - S5a : (-)-geissospermine (α - α ;208); C4c : (+)-normacusine B (α ;134), (+)-vellosimine (α ;208);
C4c - S5a : (+)-geissolosimine (α - α ;209); S4 : (+)-geissoschizoline (α ;210).

Gonioma (ALS)

G. kamassi E. Mey. : C4c : (+)-akuammidine (α ;211);
C4f : pleiocarpamine (211); C5k : fluorocarpamine (211);
E5a : (-)-eburnamine (β ;211). - *G. malagasy* Mgf.et P.B. :
C4f - P6b : (+)-14'15'-dihydro-pycnanthine (α --;212).

Haplophyton (ALS)

H. cimidum A. DC. : E5a : eburnamine (213), iso-eburnamine (213), O-methyl-eburnamine (213); P6d : (-)-cimiciphytine (214), (-)-norcimiciphytine (214).

Hazunta (TAB)

H. angustifolia Pichon (see *H. modesta* var. *methuenii* subvar. *methuenii*). - *H. coffeoides* (Boj.) Pichon (= *Tabernaemontana coffeoides* Boj.) : C5a : dregamine (215), tabernaemontanine (215), vobasine (215); J7a : ibogamine (215). - *H. costata* Mgf. : A3 : stemmadenine (215); C5a : dregamine (215), tabernaemontanine (215), vobasine

(215); J7a : ibogamine (215), isovoacangine (215). - *H. membranacea* (A. DC.) Pichon (= *Tabernaemontana membranacea* (A. DC.) Pichon) : C5a : dregamine (215), tabernaemontanine (215), vobasine (215); S4 : vincanidine (215). - *H. membranacea* (A. DC.) Pichon forma *pilifera* Mgf. : C4a : isoreserpiline (215), reserpiline (215); C5a : vobasine (215); C5c : dimethoxy-tetraphyllicine (215), monomethoxy-tetraphyllicine (215), tetraphyllicine (215), trimethoxy-tetraphyllicine (215); J7a : ibogamine (215); S4 : vincanidine (215). - *H. modesta* (Bak.) Pichon (= *Tabernaemontana modesta* Bak.) : C5a : (-)-dregamine (α ;216), (-)-tabernaemontanine (α ;216); C5a - J7a : (-)-tabernaemontanine A (217); J7a : (-)-coronaridine (β ;217), (-)-19-epi-heyneanine (β ;217), (-)-ibogamine (β ;216), (-)-voacangine (β ;217). - *H. modesta* (Bak.) Pichon var. *methuenii* (Stapf et M.L. Green) Pichon subvar. *methuenii* (= *H. angustifolia* Pichon) : C4c : normacusine B (215); C5a : dregamine (215), tabernaemontanine (215), vobasine (215); J7a : ibogamine (215), isovoacangine (215). - *H. modesta* (Bak.) Pichon var. *methuenii* (Stapf et M.L. Green) Pichon subvar. *velutina* (Pichon) Mgf. (= *H. velutina* Pichon) : C5a : (-)-dregamine (α ;218), (-)-tabernaemontanine (α ;218), (+)-voacarpine (α ;218),

(-)-vobasine (α ;218). - *H. modesta* (Bak.) Pichon
 var. *modesta* subvar. *modesta* : C4c : normacusine B
 (215); C5a : dregamine (215), tabernaemontanine (215),
 vobasine (215); J7a : ibogamine (215), isovoacangine
 (215). - *H. silicicola* Pichon : C5a : dregamine (215),
 tabernaemontanine (215), vobasine (215); J7a : iboga-
 mine (215). - *H. velutina* Pichon (see *H. modesta* var.
methuenii subvar. *velutina*).

Hedranthera (TAB)

H. barteri (Hook. F.) Pichon (= *Callichilia barteri*
 (Hook. F.) Stapf, *Tabernaemontana barteri* Hook. F.) :
C5a - J7a : (-)-voacamine (α - β ;219); C6d : (-)-loni-
 cerine (α ;220); J7a : (-)-voacangine (β ;219).

Hunteria (CAR)

H. corymbosa Roxb. (see *H. zeylanica*). - *H. eburnea*
 Pichon : C3a : (+)-dihydro-corynantheol-methochloride
 (α ;221), (-)-geissoschizol (α ;222), (+)-huntrabrine-
 methochloride (221); C4b : (+)-yohimbol-methochloride
 (α ;221); C4f : (+)-pleiocarpamine (α ;223), (+)-pleio-
 carpamine-methochloride (α ;224); C4h : (-)-burnamicine
 (α ;223); C5d : (-)-desacetyl-picraline (α ;223); C5g :

(-)-deformo-corymine (α ;222); C5p : (+)-eburnaphylline (α ;222,225,226); C6b : (-)-acetyl-corymine (α ;222), (+)-corymine (α ;222); C8a : (-)-erinicine (α ;222), (-)-erinine (α ;222); E5a : (+)-eburnamenine (β ;223,227), (-)-eburnamine (β ;223,227), (+)-eburnamonine (β ;223,227), (+)-isoeburnamine (β ;223,227); S4 : (-)-akuammicine-methochloride (α ;221); V3 : (+)-antirrhine- β -methochloride (α ;224), (+)-18,19-dihydro-antirrhine- β -methochloride (α ;224), (-)-hunterburnine- α -methochloride (α ;221), (+)-hunterburnine- β -methochloride (α ;221). - *H. elliottii* (Stapf) Pichon : C3a : huntrabrine-methochloride (228); C4a : tetrahydro-alstonine (229); C4b : yohimbol-methochloride (228); C4c : akuammidine (228); C4f : pleiocarpamine (228); C5d : desacetyl-picraline (228); C5g : (-)-deformo-corymine (α ;229), (-)-3-epi-3,17-dihydro-corymine (α ;229); C6b : acetyl-corymine (229), corymine (229); E5a : eburnamine (229), (-)-12-methoxy-14,15-dehydro-vincamine (β ;229); P3 - P3 : tetrahydro-presecamine (229); P4 : quebrachamine (229); P5 : (-)-1,2-dehydro-aspidospermidine (α ;229), (-)-vincadifformine (α ;229); P6a : (-)-kopsinine (α ;229), pleiocarpine (228); S4 : (-)-akuammicine (α ;229); V3 : hunterburnine- α -methochloride (229). - *H. umbellata* (K. Schum.) Hall. F. (= *Carpodinus umbellatus* K. Schum., *Polyadoa umbellata* Stapf, *Picralima umbellata* Stapf) : C4e - E5a : (-)-umbellamine (-- β ; 230); C6b : (+)-acetyl-corymine (α ;231), (+)-corymine (α ; 231,232); C7a : (-)-eripine (α ;233); C8a : (-)-erinicine (α ;232,234), (-)-erinine (α ;232,234), (-)-isocorymine (α ;235). - *H. zeylanica* (Retz.) Gardn. ex Thw. (= *H. corymbosa*

Roxb.) : C4c : (0)-akuammidine (α ;236); C6b : (+)-corymine (α ;237).

Lochnera (ALS)

L. lancea Boj. (ex A. DC.) K. Schum. (see *Catharanthus lanceus*). - *L. rosea* Reichb. (see *Catharanthus roseus*).

Melodinus (CAR)

M. aeneus Baill. : A4a : (+)-tubotaiwine (α ;238), (+)-tubotaiwine-N-oxide (α ;238); E5a : (+)-16-epi-14,15-dehydro-vincamine (α ;238), (+)-16-epi-14,15-dehydro-vincine (α ;238); J7a : (+)-20-epi-ibogamine (β ;238), (-)-ibogamine (β ;238); P5 : (+)-20,21-epi-aspidospermidine (239), (+)-20,21-epi-aspidospermidine-N-oxide (239), meloceline (239), melocelinine (239), (-)-11-methoxy-tabersonine (α ;238), (-)-lochnericine (α ;238), (-)-lochnerinine (α ;238), (-)-tabersonine (α ;238), (+)-vincadifformine (β ;238). - *M. australis* (F.v.Müll.) Pierre : A3 : (+)-stemmadenine (α ;240); A4a : (+)-condylocarpine (α ;240); C4c : (+)-akuammidine (α ;240). - *M. balansae* Baill. var. *paucivenosus* (S. Moore) Boiteau: C4b : (+)-renoxydine (241); C5c : (+)-ajmaline (α ;241); E5a - P5 : paucivenine (241); P6a : (-)-venalstonidine (α ;241), (-)-venalstonine (α ;241); P6f : (-)-melobaline (α ;242). -

M. buxifolius Baill. (see *M. celastroides*). - *M. celastroides* Baill. (= *M. buxifolius* Baill.): C4c : (+)-akuammidine (α ;243); E5a : 14,15-dehydro-eburnamine (244); P5 : ()-19R-hydroxy-tabersonine (α ;243), ()-19S-hydroxy-tabersonine (α ;243), (-)-tabersonine (α ;243); P6a : (-)-venalstonine (α ;243); P6b : (-)-19-epi-vindolinine (α ;243), (-)-vindolinine (α ;243). - *M. polyadenus* (Baill.) Boiteau : J9a : epi-pandoline (β ;198), (+)-pandoline (β ;198). - *M. scandens* Forst. : C4c : (+)-akuammidine (α ;245); P5 : (-)-epi-scandomeline (246), (+)-epi-scandomelonine (246), (-)-scandomeline (246), (-)-scandomelonine (246).

Munatafara (TAB)

M. sessilifolia (Bak.) Pichon : C5a : (-)-dregamine (α ;247), (-)-tabernaemontanine (α ;247); J7a : (-)-coronaridine (β ;247), (-)-eglandulosine (β ;247), (-)-6-hydroxy-3-oxo-isovoacangine (β ;247), (-)-isovoacangine (β ;247); J8c : (-)-eglandine (β ;247), (-)-3,6-oxido-isovoacangine (β ;247).

Neisosperma (RAU)

N. glomerata (Blume) Fosb. et Sach. (= *Ochrosia glomerata* (Bl.) Valetton) : C4a : reserpiline (248). - *N. lifuana* (Guill.) Boiteau (= *Ochrosia lifuana* Guill.) : C3a : 3-dehydro-ochrolifuanine (249), ochrolifuanine A (249), ochrolifuanine B (249), ochrolifuanine-N-oxide (249); C4b : (-)-decarbomethoxy-dihydro-gambirtannine (250). - *N. miana*

(Baill.ex White) Boiteau (= *Ochrosia miana* Baill.ex Guill., *O. miana* Baill.ex White) : C3a : hydroxy-ochrolifuanine (251), ochrolifuanine A (251), ochrolifuanine B (251), (-)-ochromianine (α ; 252); C4b : (-)-decarbomethoxy-dihydro-gambirtannine (250); C4d : (+)-ochromianoxine (α ; 252), - *N. nakaiana* (Koidz.) Fosb. et Sach. (= *Ochrosia nakaina* (Koidz.) Koidz. ex Hara): C3a: (+)-10-methoxy-corynantheol- β -methosalt (75, 253); C4a : 10-methoxy-serpentine (75), (+)-reserpiline (α ; 75, 253), serpentine (75, 253); C4c : (+)-akuammidine (α ; 75, 253); C5a : (-)-vobasine (α ; 75, 253). - *N. oppositifolia* (Lam.) Fosb. et Sach. (= *Ochrosia oppositifolia* (Lam.) K. Schum.) : C3a : (-)-10-methoxy-dihydro-corynantheol (α ; 254), (+)-ochrolifuanine (α ; 254), ochroposinine (255); C4a : (-)-isoreserpiline (α ; 254), (-)-isoreserpine (α ; 254), (-)-reserpiline (α ; 254), (-)-reserpinine (α ; 254). - *N. poweri* (Bailey) Fosb. et Sach. (= *Ochrosia poweri* Bailey) : C4a : (-)-isoreserpiline (α ; 256), reserpiline (257); C4b : (-)-poweridine (256), reserpine (256); C5a : (-)-ochropamine (258), (-)-ochropine (258).

Ochrosia (RAU)

O. balansae Guill. (= *Excavatia balansae* Guill.) : C4a : (-)-aricine (α ; 259), (-)-isoreserpiline (α ; 259), (-)-reserpiline (α ; 259); C5n : (-)-10,11-dimethoxy-picraphylline (α ; 259, 260). -

O. borbonica Gmel. (= *O. maculata* Jacq.) : C4b : (-)-reserpine (α ;261). - *O. coccinea* (Teysm. et Binn.) Miq. (= *Bleekeria coccinea* (Miq.) Koidz., *Excavatia coccinea* (Teysm. et Binn.) Mgf.) : C4a : reserpiline (248). - *O. compta* K. Schum. (= *O. sandwicensis* A. DC., *Bleekeria compta* (K. Schum.) Wilbur.) : C3a : (+)-ochrosandwine (α ;262); C4a : (-)-holeinine (α ;263); V3 : (+)-hunterburnine- α -methochloride (α ;262). - *O. confusa* Pichon : C3a : (-)-10-methoxy-dihydro-corynantheol (α ;264), (+)-ochrolifuanine (α ;264); C5b : (+)-carapanaubine (α ;264), (+)-rauvoxine (α ;264). - *O. elliptica* Labill. (= *Bleekeria elliptica* (Labill.) Koidz., *Excavatia elliptica* (Labill.) Mgf.) : C4a : (-)-isoreserpiline (α ;265), reserpiline (257). - *O. glomerata* (Bl.) Valetton (see *Neisosperma glomerata*). - *O. lifuana* Guill. (see *Neisosperma lifuana*). - *O. maculata* Jacq. (see *O. borbonica*). - *O. miana* Baill. ex Guill. and *O. m.* Baill. ex White (see *Neisosperma miana*). - *O. moorei* (F.v.Müll.) Koidz. : C4a : reserpiline (248). - *O. mulsantii* Montrouz (= *O. vieillardii* Guill.) : C3a : (-)-10-methoxy-dihydro-corynantheol (α ;266), (-)-ochroppsine (255); C4a : (-)-isoreserpiline (α ;266), (-)-reserpiline (α ;255); C5n : (-)-10,11-dimethoxy-picraphylline (α ;255). - *O. nakaiana* (Koidz.) Koidz. ex Hara (see *Neisosperma nakaiana*). - *O. oppositifolia* (Lam.) K. Schum. (see *Neisosperma oppositifolia*). - *O. poweri* Bailey (see *Neisosperma poweri*). - *O. sandwicensis* A. DC. (see *O. compta*). - *O. silvatica* Daen. : C4a :

isoreserpiline (267). - *O. vieillardii* Guiol. (see *O. mulsantii*). - *O. vitiensis* (Mgf.) Pichon (= *Ercavatia vitiensis* Mgf., *Bleekeria vitiensis* (Mgf.) A.C. Smith) :
C4a : (+)-bleekerine (268), holeinine (268), isoreserpiline (268); C5m : isoreserpiline-pseudoindoxyl (268).

Pagiantha (TAB)

P. cerifera Mgf. (= *Tabernaemontana cerifera* Panch. et Seb.) :
C5a : (-)-vobasine (α ;269); J7a : (-)-ibogaine (β ;270), (-)-voacangine (β ;270), (-)-hydroxyindolenine-voacangine (β ;270). - *P. heyneana* (Wall.) Mgf. (= *Tabernaemontana heyneana* Wall.) : J7a : (-)-coronaridine (β ;271), (-)-heyneanine (β ;272), (-)-ibogamine (β ;271), 3-oxo-coronaridine (271), (-)-voacangine (β ;271,273a); J8a : voacangine-pseudoindoxyl (271). - *P. macrocarpa* (Jack) Mgf. (= *Ervatamia macrocarpa* Merr., *Tabernaemontana macrocarpa* Jack) : J7a : coronaridine (273b), (-)-voacangine (β ;273b), hydroxyindolenine-voacangine (273b); P4 : conoflorine (273b). - *P. sphaerocarpa* (Bl.) Mgf. (= *Tabernaemontana sphaerocarpa* Bl.) : C5a : dregamine (274), tabernaemontanine (274).

Pandaca (TAB)

P. boiteau : C7b : methuenine (α 16); C8b : (-)-ervitsine (α ;

16). - *P. caducifolia* Mgf. : C5a : (-)-dregamine (α ; 275); J9a : (+)-20-epi-pandoline (β ; 275, 276), (+)-pandoline (β ; 275, 276), (+)-pseudotabersonine (β ; 275), (+)-20R-pseudovincadifformine (β ; 275). - *P. calcarea* (Pichon) Mgf. (= *Tabernaemontana calcarea* Pichon) : C5a : (-)-dregamine (α ; 277); J9a : (+)-pandoline (β ; 276, 277); J10a : (+)-pandine (277). - *P. crassifolia* (Pichon) Mgf. (= *Tabernaemontana crassifolia* Pichon) : J7a : (-)-ibogamine (β ; 278), (-)-tabernanthine (β ; 278). - *P. debrayi* Mgf. : C5a : (-)-dregamine (α ; 277, 278); J9a : (+)-pandoline (β ; 277); J10a : (+)-pandine (277). - *P. eusepala* Mgf. : A4a : (+)-19,20-dihydro-condylocarpine (α ; 279); C5a : (-)-vobasine (α ; 279); J7a : (-)-19-epi-vocristine (β ; 279), (-)-ibogaine (β ; 279), (+)-hydroxyindolenine-ibogaine (β ; 279); J8b : (+)-20R-dihydro-cleavamine (β ; 279), (-)-20S-dihydro-cleavamine (β ; 279); J9a : (+)-20S-1,2-dehydro-pseudoaspidospermidine (β ; 279), - *P. mauritiana* (Poiret) Boiteau : A4a : tubotaiwine (280); C5a : dregamine (277, 280), vobasine (277, 280). - *P. minutiflora* (Rich.) Mgf. : A3 : (+)-stemmadenine (α ; 281); A4a : (+)-condylocarpine (α ; 281), (+)-tubotaiwine (α ; 281); C5a : (-)-vobasine (α ; 281); J7a : (-)-coronaridine (β ; 281); P5 : (+)-vincadifformine (β ; 281). - *P. mocquersii* (A. DC.) Mgf. var. *pendula* Mgf. : J7a : (-)-coronaridine (β ; 282), (-)-19-epi-heyneanine (β ; 282), (-)-heyneanine (β ; 282), (-)-19-epi-voacristine (β ; 282), (-)-

voacristine (β ;282), (-)-voacangine (β ;282). - *P.*

ochrasceus (Pichon) Mgf. : A4a : (+)-19,20-dihydro-condylocarpine (α ;283); C4c : (+)-akuammidine (α ;283);

E5a : : (+)-16-epi-14,15-dehydro-vincamine (α ; 283); J7a : (-)-19-epi-iboxygaline (β ;283), (-)-ibogaine (β ;283), (-)-ibogaline (β ;283), (-)-19-epi-iboxygaine (β ;283); J8a : (-)-iboluteine (283); S4 : (-)-akuammicine (α ;283). - *P. retusa* (Lam.) Mgf. (= *Conopharyngia retusa* G. Don., *Plumeria retusa* Lam., *Tabernaemontana noronhiana* Boj., *T. retusa* (Lam.)

Pichon) : J7a : (-)-coronaridine (β ;278,284), (-)-heyneanine (β ;278,284), (-)-hydroxyindolenine-coronaridine (β ;278), (+)-ibogamine (α + β ; 278), 3-oxo-voacangine (284), (-)-voacangine (β ;284,285), voacristine (284). - *P. speciosa* Mgf. : C5a - J7a : (-)-decarbomethoxy-voacamine (α - β ;286); J7a : (-)-ibogaine (β ; 286), (-)-iboxygaine (β ;286), (-)-voacristine (β ;286), (-)-voacangine (β ;286); J8a : iboluteine (286). - *P. stellata* (Pichon) Mgf. (= *Tabernaemontana stellata* Pichon) : J7a : (-)-coronaridine (β ;278).

Peschiera (TAB)

P. accedens (Müll.-Arg.) (= *Tabernaemontana accedens* Müll.-Arg.):

C4c : affinisine (287); C5a - C5a : (-)-accedinine (α - α ;287), (-)-accedinisine (α - α ;287); C5a : (+)-accedine (α ;288), (+)-N-demethyl-16-epi-accedine (α ;289), (-)-N_(a)-methyl-16-epi-

affinine (α ; 288); C5a - J7a : (-)-N-demethyl-voacamine (α - β ; 287), (-)-voacamidine (α - β ; 287), (-)-voacamine (α - β ; 287), (-)-voacamine-N-oxide (α - β ; 287). - *P. affinis* (Müll.-Arg.) Miers (= *Tabernaemontana affinis* Müll.-Arg.) : C4c : affinisine (290, 291); C5a : (-)-affinine (α ; 291), vobasine (291); J7a : coronaridine (290), (-)-19-epi-heyneanine (β ; 290), heyneanine (290); J8a : coronaridine-pseudoindoxyl (290). - *P. australis* (Müll.-Arg.) Miers (= *Tabernaemontana australis* Müll.-Arg.) : C5a - J7a : voacamine (191); J7a : voacangine (191). - *P. fuchsiaeifolia* (A. DC.) Miers (= *Tabernaemontana fuchsiaeifolia* (H.B.K.) Miers) : C4c : (+)-affinisine (α ; 292), (-)-voachalotine (α ; 292). - *P. laeta* (Mart.) Miers : C3a : (-)-geissoschizol (α ; 293, 294); C4c : (+)-akuammidine (α ; 293), (+)-normacusine B (α ; 293); C5a : (-)-affinine (α ; 293), (-)-vobasine (α ; 293); C5a - J7a : (-)-conodurine (α - β ; 293), (-)-voacamine (α - β ; 293). - *P. lundii* (A. DC.) Miers : C5a : vobasine (295); J7a : coronaridine (295), (-)-19-epi-voacristine (β ; 295), ibogaine (295), iboxygaine (295), (+)-hydroxyindolenine-iboxygaine (β ; 295), voacangine (295), (-)-voacristine (β ; 295); J8a : (-)-voacristine-pseudoindoxyl (β ; 295). - *P. psychotriifolia* (H.B.K.) Miers (= *Tabernaemontana psychotriifolia* H.B.K.) : C5a : (-)-affinine (α ; 296), 16-epi-vobasinic acid (296); C5a - J7a : voacamine (191); C6c : (-)-anhydro-vobasine-diol (α ; 296, 297); J7a : coronaridine (191), voacangine (191).

Phrissocarpus (TAB)

P. rigidus Miers (see *Anacampta rigida*).

Picralima (CAR)

P. klaineana Pierre (see *P. nitida*). -

P. nitida (Stapf) Dur. (= *P. klaineana* Pierre) : C4a :

(-)-akuammigine (α ;298), (-)-melinonine A (α ;299); C4c :

(+)-akuammidine (α ; 23,300); C4e : (+)-akuammiline (α ;301),

(+)-desacetyl-akuammiline (α ;302); C5d : (-)-desacetyl-

picraline (α ;303), (-)-picraline (α ;302); C5h : akuammine

(302), (-)-pseudo-akuammigine (α ;302); C5n : (-)-picra-

phylline (α ;304); S4 : (-)-akuammicine (α ; 23), (+)-pseudo-

akuammicine (α + β ; 22). - *P. umbellata* Stapf (see *Hunteria umbellata*).

Pleiocarpa (CAR)

P. mutica Benth. : C3a : flavocarpine* (305), (+)-huntra-

brine-methochloride (306); C4c : (+)-N_(a),N_(b)-dimethyl-

sarpagine-chloride (α ;306); C4f : (+)-pleiocarpamine (α ;307),

(+) - pleiocarpamine-methochloride (α ;306); C4f - P6b : (+)-

pleiomutinine (307); E5a : eburnamenine (307), eburnamine

(307); E5a - P6a : (-)-pleiomutine (α --;308); V3 : hunter-

burnine- α -methochloride (306), (-)-hunterburnine- β -metho-

chloride (α ;306). - *P. pycnantha* (K. Schum.) Stapf (var.

pycnantha) Pichon : C4c : (+)-macusine B (α ;309); C4f : (+)-pleiocarpamine (α ;309); C4f - P5 : (+)-pycnanthinine (α - α ;309); C4f - P6b : (+)-pycnanthine (α --;309); E5a : (-)-eburnamine (β ;309). - *P. talbotii* Wernh. : C4c : (+)-normacusine B (α ;310); C5a : (-)-16-epi-affinine (α ;311); C5e : talcarpine (311); C5o : (-)-talpinine (311); D4f : (-)-3,4-dehydro-talbotine (α ;310), (-)-talbotine (α ;312), (-)-3,4,5,6-tetrahydro-talbotine (α ;312); D5b : (+)-deformyl-talbotinic acid methylester (α ;310). - *P. tubicina* Stapf : A4a : (+)-tubotaiwine (α ;313); C3a : (+)-huntrabrine-metho-chloride (313); C4c : (+)-N_(a),N_(b)-dimethyl-sarpagine-chloride (α ;313), (+)-macusine B (α ;313); C4f - P5 : (+)-pycnanthinine (α - α ;314); E5a : (-)-eburnamine (β ;314); E5a - P6a : (-)-pleiomutine (α --; 313); S4 : (-)-19,20-dihydro-akuammicine (α ;313), (-)-tubifolidine (α ;313), (-)-tubifoline (α ;313).

Plumeria (ALS)

P. retusa Lam. (see *Pandaca retusa*).

Polyadon (CAR)

P. umbellata Stapf (see *Hunteria umbellata*).

Rauvolfia (RAU)

R. affinis Müll.-Arg. (see *R. grandiflora*). - *R. amsoniae-folia* (Miq.) A. DC. : C4a : ajmalicine (315), aricine (315); C4b : deserpidine (315), rescinnamine (315), reserpine (315), methyl reserpate (315), yohimbine (315). - *R. bahiensis* A. DC. : C4a : reserpiline (316); C4b : rescinnamine (316), reserpine (316). - *R. beddomei* Hook. F. : C4a : (-)-ajmalicine (α; 5a); C4c : (+)-sarpagine (α; 5a). - *R. boliviana* Mgf. (see *R. schuelii*). - *R. caffra* Sond. (= *R. natalensis* Sond., *R. welwitschii* Stapf) : C4a : ajmalicine (317), reserpiline (317), serpentine (317,318), tetrahydroalstonine (318); C4b : rescinnamine (317), reserpine (317,319); C4c : sarpagine (318); C5c : (+)-ajmaline (α; 317,318,319), raucaffricine (320); D6b : raucaffrinoline (321), (+)-perakine (318); D6c : peraksine (318). - *R. cambodiana* Pierre ex Pitard : C4a : aricine (322), (-)-isoreserpiline (α;323), reserpiline (322); C4b : (-)-reserpine (α;323); C5a : pelirine (322); C5c : ajmaline (322). - *R. canescens* L. (see *R. tetraphylla*). - *R. capuroni* Mgf. : C4b : (+)-11-methoxy-pseudoyohimbine (α;324), (+)-11-methoxy-yohimbine (α;324). - *R. chinensis* (Hance) Hemsl. : C4a : ajmalicine (5a), C4b : reserpine (5a); C5c : ajmaline (5a). - *R. confertiflora* Pichon : C4a : isoreserpiline (325), (+)-raufloridine (α;325), reserpiline (325), (-)-reserpiline-methosalt (α;326),

tetraphylline (325), tetraphyllinine (325); C4b : reserpine (325); C4e : (+)-rauflorescine (327); C5c : ajmaline (325), mauiensine (325), quebrachidine (325), (+)-rauflorescine (325), tetraphyllicine (325). - *R. cubana* A. DC. : C4a : reserpiline (316); C4b : deserpidine (316), rescinnamine (316), reserpine (316). - *R. cumminsii* Stapf : C3a : ()-corynantheol (α ; 328,329), ()-corynantheol (α ; 328,329,330); C4a : ajmalicine (328,331), ajmalicinine (328,330), aricine (328,331), 10,11-dimethoxy-ajmalicine (328,330), 19-epi-serpentine (328,331), serpentine (328,331); C4b : 18-hydroxy-yohimbine (328,330), rescinnamine (328,331), reserpine (328,331), yohimbine (328,331), α -yohimbine (328,331); C4c : O-methyl-normacusine B (328,329,330), O-methyl-normacusine B-N-oxide (328,330), normacusine B (328,330), pericyclivine (328), sarpagine (328); C5c : ajmaline (328), (O)-N_a-demethyl-purpeline (α ; 332), N_a-demethyl-dihydro-purpeline (α ; 332), diacetyl-ajmaline (328), dihydro-norpurpeline (328,330), endolobine (328,329), normitoridine (328,329), norpurpeline (328,330), norseredamine (328), nortetraphyllicine (328,330), purpeline (328,330), seredamine (328,330), tetraphyllicine (328), 17-O-trimethoxybenzoyl-seredamine (328), vomalidine (328); C5d : ()-desacetyl-picraline (α ; 330), (-)-picrinine (α ; 329); C5n : 20-epi-picraphylline (328); D6c : peraksine (330). - *R. decurva* Hook. F. : C4a : (-)-isoreserpiline (α ; 333), (-)-reserpiline (α ; 333), reserpinine (333); C4b : rescinnamine

(333), (-)-reserpine (α ;333); C4c : (+)-sarpagine (α ; 333). - *R. degeneri* Sherff : C3a - C4a : serpentinine (334); C4a : tetraphylline (334); C5c : (+)-ajmaline (α ;334), tetraphyllicine (334). - *R. densiflora* (Thw.) Benth. et Hook. : C4a : reserpinine (5a); C4b : reserpine (335); C4c : sarpagine (5a); C5c : ajmaline (335). - *R. discolor* Pichon : C4a : (-)-isoreserpiline (α ; 89,336), (-)-reserpiline (α ;337), tetraphylline (336,338), (-)-tetraphyllinine (336); C4b : (-)-reserpine (α ;337); C5a : (-)-16-decarbomethoxy-19,20-dihydro-vobasine (α ;339), (-)-tabernaemontanine (α ;336 340); C5c : (+)-quebrachidine (α ;336). - *R. fruticosa* Burck : C4a : ajmalicine (5a), aricine (5a), serpentine (5a); C4b : yohimbine (5a), α -yohimbine (5a); C5c : ajmaline (5a). - *R. grandiflora* Mart. (= *R. affinis* Müll.-Arg.) : C4a : reserpiline (316), reserpinine (316); C4b : deserpidine (316), pseudoreserpine (5a), raugustine (5a), raunescine (5a), rescinnamine (316), reserpine (144). - *R. heterophylla* R. et Sch. (see *R. tetraphylla*). - *R. hirsuta* Jacq. (see *R. tetraphylla*). - *R. indecora* Woods. (see *R. ligustrina*). - *R. inebrians* K. Schum. : C4a : ajmalicine (316), reserpiline (316); C4b : rescinnamine (316), reserpine (316). - *R. lamarkii* A. DC. (see *R. virides*). - *R. ligustrina* R. et Sch. (= *R. indecora* Woods., *R. ternifolia* H.B.K.): C3a - C4a : serpentinine (341); C4a : ajmalicine (341), aricine (341),

isoreserpiline (341), isoreserpinine (341), reserpiline (316), reserpinine (316), serpentine (341), tetrahydroalstonine (341); C4b : deserpidine (316), isopseudoreserpine (5b), isoraunescine (341), isoreserpine (341), pseudoreserpine (341), (-)-raugustine (α ; 341), raunescine (341), renoxydine (341), rescinnamine (316), reserpine (316), yohimbine (341), α -yohimbine (341); C4c : sarpagine (341); C5c : ajmaline (341); C5m : (-)-isoreserpiline-pseudoindoxyl (α ; 5a). - *R. littoralis* Pierre (see *R. macrocarpa* Standl.). - *R. longecuminata* De Wild. et Dur. : C4b : reserpine (342). - *R. longifolia* A. DC. (see *Tonduzia longifolia*). - *R. macrocarpa* Standl. (= *R. littoralis* Pierre) : C4a : reserpiline (316); C4b : reserpine (316). - *R. macrophylla* Stapf : C4a : ajmalicine (343), serpentine (343); C4b : rescinnamine (343), reserpine (343), yohimbine (343); C5c : ajmaline (343), norajmaline (343). - *R. manni* Stapf : C4b : reserpine (5a); C5c : (-)-vincamajine (α ; 344). - *R. matfeldiana* Mgf. : C4a : reserpiline (5a); C4b : pseudoreserpine (5a), raugustine (5a). - *R. mauensis* Sherff : C3a - C4a : serpentinine (334); C5c : ajmalidine (345), (+)-mauiensine (α ; 334), (+)-sandwicine (α ; 334), tetraphyllicine (334). - *R. micrantha* Hook. F. : C4a : ajmalicine (346), reserpiline (5a); C4b : reserpine (346); C4c : neosarpagine (5a); C5c : ajmaline (5a). - *R. mombasiana* Stapf : C3a : corynantheol (347); C4a : (-)-ajmalicine (α ; 347),

reserpiline (316); C4b : rescinnamine (316), reserpine (316), yohimbine (347); C4c : normacusine B (347); C5c : ajmaline (5a), endolobine (347), norpurpeline (347), (+)-purpeline (α ;347); D6c : peraksine (347). - *R. nana* Bruce : C4b : reserpine (5a). - *R. natalensis* Sond. (see *R. caffra*). - *R. nitida* Jacq. : C4a : ajmalicine (348), aricine (348), isoreserpiline (348), (-)-isoreserpinine (α ;348), (-)-rauniticine (α ;348), (-)-raunitidine (α ;348), reserpiline (316), reserpinine (348); C4b : (-)-deserpideine (α ;349), (-)-deserpidine (α ;349), rescinnamine (316), reserpine (316). - *R. obscura* K. Schum. : C3a : 10-methoxy-geissoschizol (350); C4a : (+)-alstonine (α ;342,351,352), tetrahydroalstonine (351); C4b : 19,20-dehydro-yohimbine (353), deserpidine (351), methyl deserpidate (351), methyl reserpate (351), rescinnamine (351), reserpine (351), α -yohimbine (350,351); C5c : ajmaline (351), 12-methoxy-ajmaline (351), norajmaline (351), rauvomitine (351), tetraphyllicine (351), 17-O-(3',4',5')-trimethoxybenzoyl-ajmaline (351), vomalidine (351). - *R. oreogiton* Mgf. (= *R. volkensii* Stapf) : C4a : ajmalicine (354), reserpiline (354), serpentine (354); C4b : renoxydine (354), rescinnamine (354), reserpine (354), α -yohimbine (354); C5c : ajmaline (354). - *R. paraensis* Ducke : C4a : reserpiline (316); C4b : rescinnamine (316), reserpine (316). - *R. pentaphylla* (Hub.) Ducke : C4a : ajmalicine (316), reserpiline (316), reserpinine (316);

C4b : deserpidine (316), rescinnamine (316), reserpine (316). - *R. perakensis* King et Gamble : C4a : aricine (355), (-)-isoreserpiline (α ;355); C4b : reserpine (355), α -yohimbine (356); C4c : normacusine B (356), (+)-sarpagine (α ;355); C5a : (-)-pelirine (355); C5c : (+)-ajmaline (α ;355), 1-demethyl-17-O-acetyl-desoxy-ajmaline-diene-(1,19) (356); D6b : (+)-perakine (α ;355); D6c : (+)-peraksine (α ;356). - *R. reflexa* Tejasm. et Binn. : C5c : purpeline (357), (+)-reflexine (α ;357). - *R. rosea* K. Schum. : C4a : ajmalicine (316), deserpidine (316), rescinnamine (316), reserpiline (316); C4b : reserpine (316). - *R. salicifolia* Griseb. : C4a : reserpiline (316); C4b : deserpidine (316), rescinnamine (316), reserpine (316). - *R. sandwicensis* A. DC. : C3a - C4a : serpentinine (334); C4a : reserpiline (316), tetraphylline (334); C4b : reserpine (316); C5c : (+)-sandwicine (α ;334), tetraphyllicine (334). - *R. sara-piquensis* Woods. : C4b : reserpine (358). - *R. schuelii* Speg. (= *Aspidosperma spegazzini* Molf. ex Meyer, *R. boliviana* Mgf.) : C4a : (-)-aricine (α ;359), (-)-isoreserpiline (α ;359), (-)-reserpiline (α ;359); C4b : (-)-reserpine (α ;359); C4c : (+)-N_(b)-methyl-akuammidine-chloride (α ;360), (+)-spetrine (α ;360); C5c : (+)-ajmaline (α ;360). - *R. sellowii* Müll.-Arg. : C4a : (-)-ajmalicine (α ;361), (-)-aricine (α ;361), serpentine (5a), (-)-tetrahydroalstonine

(α ;361); C4b : (-)-reserpine (α ;361); C5c : ajmalidine (361), (+)-ajmaline (α ;361), (+)-tetraphyllicine (α ;361). - *R. serpentina* (L.) Benth. : C3a - C4a : (+)-serpentinine (362); C4a : (-)-ajmalicine (α ;362), (-)-reserpiline (α ;362), (-)-reserpinine (α ;362), (+)-serpentine (α ;362); C4b : (-)-corynanthine (α ;362), deserpidine (363), (-)-isorauhimbine (α ;364), (-)-methyl reserpate (α ;362), raunescine (5a), (-)-rescinamine (362,363), renoxydine (365), (-)-reserpine (α ;362,363), (+)-yohimbine (α ;366), (-)- α -yohimbine (α ;362); C4c : (+)-sarpagine (α ;362); C5c : (+)-ajmaline (α ;362), (+)-isoajmaline (α ;362), tetraphyllicine (362); C5g : (-)-rauwolfinine (367). - *R. sprucei* Müll.-Arg. : C4a : reserpiline (316); C4b : deserpidine (316), rescinnamine (316), reserpine (316). - *R. suaveolens* S. Moore : C5e : (O)-suaveoline (369). - *R. sumatrana* (Miq.) Jack : C3a - C4a : serpentinine (368); C4a:ajmalicine (368), aricine (368), reserpiline (316), serpentine (368); C4b : rescinnamine (316), reserpine (316), yohimbine (368), α -yohimbine (368); C5c : ajmaline (368), (+)-N_(a)-demethylseredamine (α ;368). - *R. ternifolia* H.B.K. (see *R. ligustrina* R. et Sch.). - *R. tetraphylla* L. (= *R. canescens* L., *R. heterophylla* R. et Sch., *R. hirsuta* Jacq.) : C3a - C4a : serpentinine (370); C4a : (-)-ajmalicine (α ; 371), alstonine (372), (-)-aricine (α ;373,374), (-)-isoreserpiline

(α ;374), (-)-isoreserpinine (α ;374), (-)-reserpiline (α ;373, 374), (-)-reserpinine (α ; 371), serpentine (375), (-)-tetraphylline (370); C4b : (+)-canembine (5a), corynanthine (5a), (-)-deserpidine (α ;363), (-)-isoraunescine (376), (-)-pseudoreserpine (377), (+)-pseudoyohimbine (α ;370), (-)-raunescine (376), (-)-raujemidine (378), renoxydine (365), (-)-reserpine (α ;373), (-??(375))-yohimbine (α ;375), (-)- α -yohimbine (α ;373,374), (-)- β -yohimbine (α ;379); C4c : (+)-sarpagine (α ;371); C5c : (+)-ajmaline (α ;371), (+)-tetraphyllicine (α ;370). - *R. verticillata* (Lour.) Baill. : C4a : (-)-ajmalicine (α ;380), aricine (5b), serpentine (381); C4b : (-)- reserpine (α ;381), yohimbine (381); C4c : (+)-vellosimine (α ;382); C5c : ajmaline (381); D6c : (+)-peraksine (α ;382). - *R. viridis* R. et Sch. (= *R. lamarkii* A. DC.) : C4a : reserpiline (316), reserpinine (316); C4b : deserpidine (316), rescinnamine (316), reserpine (316). - *R. volkensii* Stapf (see *R. oreogiton*). - *R. vomitoria* Afz. : C3a : geissoschizol (383), 10-hydroxy-geissoschizol (384), 10-methoxy-geissoschizol (384); C3a - C4a : serpentinine (5a); C4a : ajmalicine (5a), (+)-alstonine (α ;352), (-)-aricine (α ;385, 386), 19,20-dehydro-reserpiline (384), (-)-isoreserpiline (α ; 385,387), (+)-raumitorine (α ;388), (+)-rauvanine (α ;388), (-)-reserpiline (α ;384,386,389), tetrahydroalstonine (385); C4b : deserpidine (363), 18-hydroxy-yohimbine (384), methyl

reserpate (384), rescinnamine (386), (-)-renoxydine (α ; 365), (-)-rescidine (5a), (-)-reserpine (α ;390), (-)-seredine (391), (+)-yohimbine (α ;384,392), (-)- α -yohimbine (α ;386,392); C4c : normacusine B (384), (+)-sarpagine (α ;384,387); C4e : (+)-desacetyl-deformo-akuammiline (α ;393); C5b : (-)-carapanaubine (α ;384,385, 386), carapanaubine-N-oxide (386), isocarapanaubine (384), (+)-rauvoxine (α ;386,394), (+)-rauvoxinine (α ;394); C5c : (+)-17-acetyl-ajmaline (α ;395), ajmaline (386), N_(a)-demethyl-rauvomitine (386), 10-hydroxy-nortetraphyllicine (384), indolenine RG (384), isoajmaline (5a), isosandwicine (386), (+)-mitoridine (α ;386,396), norpurpeline (384), norseredamine (384), nortetraphyllicine (384), (+)-purpeline (α ;384,386,396), (-)-rauvomitine (α ;386,396), sandwicine (386), (+)-seredamine (α ;386), tetraphyllicine (386), (+)-vomalidine (α ;397), (-)-vomilenine (α ; 398); C5d : (-)-picrinine (α ; 393); C5e : suaveoline (386); C5m : (-)-isoreserpiline-pseudoindoxyl (α ;384,386); D6c : (+)-peraksine (α ;383). - *R. welwitschii* Stapf (see *R. affra* Sond.). - *R. yunnanensis* Tsiang : C4a : ajmalicine (5b); C4b : reserpine (5b).

Rejoua (TAB)

R. aurantiaca Gaud. : J7a : voacangine (399); J8a : iboluteine (399), (-)-voaluteine (399).

Rhazya (ALS)

R. orientalis A. DC. : D3a : (-)-5 α -carboxy-strictosidine (α ;400), (-)-strictosidine (α ;401). - *R. stricta* Decaisne : C3a : (+)-geissoschizine (α ;402); C4c : (O)-akuammidine (α ;108); (O)-akuammidine- methosalt (α ;300); C4e : (+)-rhazinaline (402), (-)-strictalamine (α ;403); (+)-strictamine (α ;403); D3a : (-)-strictosidine (α ;401); E5a : eburnamenine (108), eburnamine (108), eburnamonine (108); S4 : (-)-nor-fluorocurarine (α ;403), (-)-sewarine (α ; 403,404,405); V3 : (-)-antirrhine (α ;406); V4 : (-)-strictosamide (α ;406).

Schizogygia (TAB)

S. coffaeoides (Boj.) Baill. : E5b : (-)-schizophylline (407, 408); E6a : (-)-isoschizogaline (407, 408), (-)-isoschizogamine (407, 408), (+)-schizogaline (407, 408), (-)-schizogamine (407, 408), (+)-schizogygine (407), (+)- α -schizogygol (407,408).

Stemmadenia (TAB)

S. donnell-smithii (Rose) Woods. : A3 : (+)-stemmadenine (α ; 188, 409); C5a - J7a : (-)-voacamine (α - β ;409); J7a : (-)-coronaridine (β ;410), (-)-isovoacangine (β ;409), (-)-tabernanthine (β ;409), (-)-voacangine (β ;409). - *S. galeottiana*

(A. Rich.) Miers. : J7a : (-)-ibogamine (β ;409). -

S. obovata (Hook. et Arn.) K. Schum. : A3 : stemmadenine (410); C4a : (-)-ajmalicine (α ;410); J7a : coronaridine (410), voacangine (410). - *S. tomentosa* Greenman var. *palmeri* (Rose) Woods. : A3 : stemmadenine (410), J7a : coronaridine (410).

Stenosolen (TAB)

S. heterophyllus (Vahl.) Mgf. (= *Tabernaemontana heterophylla* Vahl.) : P5 - J10d : (+)-ervafoline (α - β ;411).

Tabernaemontana (TAB)

T. accedens Müll.-Arg. (see *Peschiera accedens*). - *T. affinis* Müll.-Arg. (see *Peschiera affinis*). - *T. alba* Mill. : J7a : coronaridine (410). - *T. armeniaca* : P6e : apodine (412), desoxo-apodine (413). - *T. australis* Müll.-Arg. (see *Peschiera australis*). - *T. barteri* Hook. F. (see *Hedranthera barteri*). - *T. brachyantha* Stapf (see *Conopharyngia brachyantha*). - *T. calcarea* Pichon (see *Pandaca calcarea*). - *T. cerifera* Panch. et Seb. (see *Pagiantha cerifera*). - *T. chartacea* Pichon (see *Gabunia eglandulosa*). - *T. citrifolia* L. (= *T. oppositifolia* (Spr.) Urb.) : C5a - J7a : voacamine (191); J7a : coronaridine (191), ibogamine (191), voacangine (191). - *T. coffeoides* Boj.

(see *Hazunta coffeoides*). - *T. contorta* Stapf 1894
 (see *Conopharyngia contorta*). - *T. coronaria* R. Br.
 (see *Ervatamia coronaria*). - *T. crassa* Benth. (see
Conopharyngia crassa). - *T. crassifolia* Pichon (see
Pandaca crassifolia). - *T. cumminsii* (see *Conopharyngia*
cumminsii). - *T. divaricata* R. Br. (see *Ervatamia di-*
varicata). - *T. eglandulosa* (Stapf) Pichon (see
Gabunia eglandulosa). - *T. elegans* Stapf (see *Cono-*
pharyngia elegans). - *T. fuchsiaeifolia* (A. DC.) Miers
 (see *Peschiera fuchsiaeifolia*). - *T. heterophylla* Vahl.
 (see *Stenosolen heterophyllus*). - *T. heyneana* Wall.
 (see *Pagiantha heyneana*). - *T. holstii* K. Schum. : A4a :
 (+)-tubotaiwine-N-oxide (α ;414); C4c : perycyclivine
 (415); C5a : perivine (415), vobasine (415); C5a - J7a :
 conoduramine (415), conodurine (415), gabanine (415),
 19-oxo-conodurine (415); J7a : coronaridine (415), 19-
 oxo-coronaridine (415). - *T. johnstonii* Pichon (see
Conopharyngia johnstonii). - *T. jollyana* (Stapf) Pichon
 (see *Conopharyngia jollyana*). - *T. killipii* Woods. (see
Bonafousia killipii). - *T. laevis* Vell. (see *Geissospermum*
vellosii). - *T. laurifolia* L. : J7a : coronaridine (416),
 ibogamine (416), iboxygaine (416), isovoacangine (416),
 (-)-isovoacristine (β ;416), tabernanthine (416). - *T.*
macrocarpa Jack. (see *Pagiantha macrocarpa*). - *T. macro-*
phylla Miers (see *Anacampta rigida*). - *T. membranacea*

(A.DC.) Pichon (see *Hazunta membranacea*). - *T. modesta* Bak. (see *Hazunta modesta*). - *T. mucronata* Merr. (see *Ervatamia mucronata*). - *T. noronhiana* Boj. (see *Pandaca retusa*). - *T. odoratissima* (Stapf) Pichon (see *Gabunia odoratissima*). - *T. oppositifolia* (Spr.) Urb. (see *T. citrifolia*). - *T. orientalis* R. Br. (see *Ervatamia orientalis*). - *T. pachysiphon* Stapf (see *Conopharyngia cumminsii*). - *T. pandacaqui* Poir. (see *Ervatamia pandacaqui*). - *T. penduliflora* K. Schum. (see *Conopharyngia penduliflora*). - *T. psychotriifolia* (H.B.K.) Miers (see *Peschiera psychotriifolia*). - *T. retusa* (Lam.) Pichon (see *Pandaca retusa*). - *T. rigida* Miers. (see *Anacampta rigida*). - *T. rupicola* Benth. (see *Anacampta rupicola*). - *T. sphaerocarpa* Bl. (see *Pagiantha sphaerocarpa*). - *T. stellata* Pichon (see *Pandaca stellata*). - *T. undulata* : J7a : coronaridine (417).

Tabernanthe (TAB)

T. iboga Baill. (418): J7a : (-)-coronaridine (β ;419), (+)-hydroxyindolenine-ibogaine (β ;420), (+)-hydroxyindolenine-ibogamine (420), (-)-ibogaine (β ;420) (-)-ibogaline (β ;418), (-)-ibogamine (β ;420), (-)-iboxygaine (β ;420), (-)-isovoacangine (β ;418), (-)-tabernanthine (β ;420), (-)-voacangine (β ;420); J8a : demethoxy-iboluteine (420), (-)-iboluteine (420,421); J8d : (-)-kisantine (420); J10b : (+)-iboxy-

phylline (β ;422); J10c : (+)-ibophyllidine (β ; 422). -
T. subsessilis Stapf : J7a : (-)-ibogamine (β ; 422);
J10b : (+)-iboxyphylline (β ;422); J10c : (+)-ibophyllidi-
 ne (β ;422).

Tonduzia (ALS)

T. longifolia (A.DC.) Mgf. (= *Rauwolfia longifolia* A.DC.) :
C4a : ajmalicine (316); C4b : deserpidine (423), rescinnamine
 (316), reserpine (316); C5c : ajmaline (423), (-)-vinca-
 majine (α ;424).

Vallesia (RAU)

V. dichotoma R. et P. : A4a : (-)-N_(a)-acetyl-aspidosperma-
 tidine (α ;425), condylocarpine (425), (+)-19,20-dihydro-
 condylocarpine (α ;425); A4b : precondylocarpine (425); A6 :
 (+)-dichotine (α ;426,427), (+)-11-methoxy-dichotine (α ;426,427);
C4b : reserpine (428); C4c : (+)-akuammidine (α ;425); C4f :
 pleiocarpamine (425); E5b : (-)-vallesamidine (β ;429); V3 :
 (+)-vallesiachotamine (α ;430).

Vinca (ALS)

V. difformis Pourr.: C4c : (+)-akuammidine (α ; 431,432),
 (+)-sarpagine (α ; 433), (+)-vellosimine (α ;431); C5a :
 (-)-vincadifline (α ;434); C5c : (-)-vincamedine (α ;431,435),

vincamajine (α ;431,435); E5a : (+)-vincamine (α ;436). -
V. elegantissima Hort.: C4a : reserpinine (437); C4c :
 lochnerine (438); C5b : (+)-elegantissine (α ; 438), (+)-
 isoelegantissine (α ;438), (-)-isomajdine (α ; 437,438),
 (-)-majdine (α ;438); C5c : vincamajoreine (438). - *V.*
erecta Rgl. et Schmalh. : C4a : ajmalicine (5a), ervine
 (5a), reserpinine (5a); C4c : akuammidine (5b), (+)-
 O-benzoyl-tombozine (α ;439), (+)-ervincidine (440), nor-
 macusine B (441); C5b : (-)-N-acetyl-vinerine (α ; 442,443),
 ericinine (444), (-)-majdine (α ;445), (+)-vineridine (α ; 442,
 443), (+)-vineridine-N-oxide (α ;446), (+)-vinerine (α ; 443),
 ()-vinerine-N-oxide (α ;447), (-)-vinerinine (448); C5c :
 10-methoxy-vinorine (449), (+)-vincarine (α ;450); C5d :
 (O)-vincaricine (451), (-)-vincaridine (451,452), (-)-
 vincarinine (453); C5h : akuammine (5b), O-methyl-akuammine
 (454); E5a : (-)-eburnamonine (α ;455), (+)-vincamine (α ; 436),
 vincine (456); P6a : maidinine (447); S4 : (-)-akuammicine
 (α ;457), (-)-norfluorocurarine (α ;458), (-)-vincanicine (459,
 460), (-)-vincanidine (α ;459,461), (-)-vinervine (α ; 457,461),
 (-)-vinervinine (441,459). - *V. herbacea* W. et K. : C3a :
 (-)-hervine (α ;462); C4a : (-)-herbaceine (α ;463), (-)-
 herbaine (464), isoreserpinine (465), reserpinine (5b);
C5b : (-)-herbaine (α ;466), herboxine (467), (-)-isomajdine
 (α ;468,469), (-)-majdine (α ;468,469); C5c : herbadine (470),

herbamine (470), vincarine (471); S4 : (-)-norfluorocaraine (α ;468). - *V. lancea* (see *Catharanthus lanceus*.) - *V. libanotica* Zucc. : C4a : (-)-rauniticine (α ;472), (-)-reserpinine (α ;472); C4e : (+)-strictamine (α ;472); C5c : herbadine (473), (-)-herbamine (α ;472,474), (+)-quebrachidine (α ;472), (-)-vincamajine (α ;472); C5d : picrinine (472); P6f : (-)-vincoline (α ;472). - *V. major* L. (= *V. pubescens* Urv.) : C4a : ervine (5b), (-)-reserpinine (α ;475), serpentine (5a), tetrahydroalstonine (5a); C4c : sarpagine (5a); C5b : alkaloid V (476), (-)-carapanaubine (α ;477), (-)-isomajdine (α ;469), (-)-majdine (α ;469,475); C5c : (-)-majoridine (α ;478,479), (-)-vincamajine (α ;478), (-)-vincamedine (α ; 5b); C5h : (-)-akuammine (α ;475); E5a : (+)-vincamine (α ;436), (+)-vincine (α ;476,480); S4 : akuammicine (5b), (-)-norfluorocurarine (α ; 5b). - *V. major* L. var. *major* : C4a : (-)-reserpinine (α ;481); C4c : lochvinerine (481), majvinine (482), (+)-10-methoxy-vellosimine (α ;481,483); C5c : (-)-majoridine (α ;481,484), vincamajoreine (481). - *V. minor* L. : C4b : reserpine (5b); C4e : (+)-akuammiline (α ; 485), desacetyl-akuammiline (485), (+)-10-methoxy-desacetyl-akuammiline (α ;485), (-)-strictamine (α ;486); C5c : ()-vinorine (α ;487); C5d : picrinine (488); C5g : (-)-vincoridine (α ;489),(-)-vincorine (α ;114,490); C5y : (-)-vinoxine

(491); E5a : (+)-eburnamenine (β ;492), (-)-eburnamine (β ;492), (-)-eburnamonine (α ;492), (+)-eburnamonine (α + β ;492), (-)-16-epi-vincamine (α ;493), (+)-isoeburnamine (β ;492), (-)-11-methoxy-eburnamonine (494), (+)-vincamine (α ; 152), (+)-vincaminine (α ;495), (+)-vincine (α ;496), (+)-vincinine (α ;495). - *V. pusilla* Murr. (see *Catharanthus pusillus*). - *V. rosea* (L.) Reichb. (see *Catharanthus roseus*).

Voacanga (TAB)

V. africana Stapf : C4b : isorauhimbine (497), pseudo-yohimbine (497), reserpine (497), β -yohimbine (497); C5a : vobasine (497); C5a - J7a : 18'-decarbomethoxy-voacamine (497), (-)-voacamidine (α - β ;166), (-)-voacamine (α - β ;497,498), (-)-voacamine-N-oxide (α - β ;499), (-)-voacordine (α - β ;498); D6b : perakine (497); J7a : coronaridine (497), ibogaine (497), ibogamine (497), iboxygaine (497), voacangine (497), hydroxyindolenine-voacangine (497,500), voacangine-lactam (497), (-)-voacristine (β ;501), (+)-voacryptine (β ; 502); J8a : iboluteine (497). - *V. bracteata* Stapf var. *bracteata* : C5a - J7a : (-)-19-epi-voacordine (α - β ;503,504), (-)-voacamine (α - β ; 503,504), (-)-voacamine-N-oxide (α - β ; 505), (-)-voacordine (α - β ;503,504); J7a : (-)-19-epi-voacristine (β ;503,504), (-)-voacangine (β ;503,504);

(-)-voacristine (β ; 503,504). - *V. chalotiana* Pierre ex Stapf : C4a : (-)-tetrahydroalstonine (α ;506); C4c : (-)-17-O-acetyl-19,20-dihydro-voachalotine (α ;507), (+)-akuammidine (α ;508), (+)-3-hydroxy-voachalotine (506), 21-hydroxy-voachalotine (508), polynuridine (508), (-)-voachalotine (α ; 509); C5a : (+)-voacarpine (α ;510); C5f : (-)-voachalotine-oxindole (α ;508); C5i : (+)-dehydro-voachalotine (α ;506,511); C5o : (-)-voacoline (α ; 512); E5a : (+)-14,15-dehydro-vincamine (α ; 506); E6c : (-)-cuanzine (α ;506,513), (-)-decarbomethoxy-apocuanzine (α ;506,514). - *V. dregei* E.M. (see *V. thouarsii*). - *V. globosa* (Blanco) Merr. : C5a : tabernae-
montanine (156); C5a - J7a : (-)-voacamine (α - β ;515); J7a : (-)-voacangine (β ;515); P6e - P6e : (-)-quimbeline (516). - *V. grandiflora* Miq. : P6e - P6e : (-)-amataine (α - α ;120). - *V. grandifolia* (Miq.) Rolfe : C4c : (+)-akuammidine (α ;517); C5a - J7a : (-)-voacamine (α - β ; 518); J7a : (-)-voacangine (β ;518); P6e - P6e : (-)-amataine α - α ;120). - *V. megacarpa* Merr. : C5a - J7a : voacamine (5b). - *V. papuana* (F.v.Müll.) Boerl. : C5a - J7a : voacamine (519); J7a : voacangine (519). - *V. schweinfurthii* Stapf : C5a - J7a : (-)-voacamine (α - β ;520), voacarine (521); J7a : voacangine (5b). - *V. thouarsii* R. et Sch. var. *dregei* (E.Mey.) Pichon (= *V. dregei* E. Mey., *V. thouarsii* R. et Sch. var. *obtus*a (K. Schum.) Pichon, *V. thouarsii*

R. et Sch.): C5a : (-)-dregamine (α ;522), (-)-vobasine (α ;523); C5a - J7a : 18'-decarbomethoxy-voacamine (523), (-)-voacamine (α - β ; 523), voacorine (5b); J7a : conopharyngine (5b), ibogaine (523,524), (-)-voacangine (β ; 523, 524,525), (-)-voacristine (β ;523,524); J8a : iboluteine (523), (-)-voaluteine (523); P6e - P6e : 12-O-demethyl-vobtusine (526), 2'-desoxy-vobtusine-lactam (526), (-)-subsessiline-lactone (α - α ;527), (-)-vobtusine-3-lactam-N-oxid (α - α ; 526), (-)-vobtusine-3-lactam (α - α ;524,526).

LOGANIACEAEGardneria (STR)

G. angustifolia Wall. (= *G. shimadai* Hayata) : C5f :
 (-)-chitosenine (α ;528); C5f - C6a : (-)-gardmultine
 (528); C6a : (-)-18-demethyl-gardneramine (α ;528), (-)-
 gardneramine (α ;528,529). - *G. insularis* Nakai (see
G. nutans). - *G. multiflora* Makino : C5f : alkaloid I
 (75), alkaloid J (75), alkaloid L (75), alkaloid M
 (75), alkaloid N (75), (-)-chitosenine (α ; 528,530);
C5f - C6a : (-)-gardmultine (528,531); C6a : 18-demethoxy-
 gardfloramine (530), (-)-18-demethoxy-gardneramine (530),
 (-)-18-demethyl-gardneramine (α ;528,529), (-)-gardfloramine
 (530), (-)-gardneramine (α ;528,529,532), gardneramine-N-oxide
 (75). - *G. nutans* Sieb. et Zucc. (= *G. insularis* Nakai) :
C4c : (-)-gardnerine (α ;528,533,534,535); C5i : (+)-gard-
 nutine (α ; 528,533,535), (+)-18-hydroxy-gardnutine (α ; 528,
 533, 535); C6a : (-)-18-demethyl-gardneramine (α ; 536),
 (-)-gardneramine (α ;529). - *G. shimadai* Hayata (see *G. an-*
gustifolia).

Gelsemium (GEL)

G. elegans Benth.: C4b : sempervirine* (537). - *G. semper-*
virens (L.) Aiton : C4b : sempervirine* (5a).

Mostuea (GEL)

M. buchholzii Engl. : C4b : sempervirine* (538). -

M. stimulans A. Chev. : C4b : sempervirine* (538).

Strychnos (STR) (582)

Calebassen-Curare : C4c : (+)-lochneram (α ;539), (+)-lochnerine (α ;539), (+)-macusine B (α ;540); C4f : (+)-C-mavacurine (α ; 75,541), C-profluorocurine (5a); C5k : (+)-C-fluorocurine (α ;541); S4 : (-)-C-fluorocurarine (α ; 5a); S4 - S4 : (+)-C-alkaloid A (α - α ; 5), (-)-C-alkaloid D (α - α ; 5), ()-C-alkaloid E (α - α ; 5), ()-C-alkaloid F (α - α ; 5), ()-C-alkaloid G (α - α ; 5), (-)-C-alkaloid H (α - α ; 5), (+)-C-calebassine (α - α ; 5), (+)-C-curarine I (α - α ; 5), (-)-C-dihydrotoxiferine (α - α ; 5), (-)-C-toxiferine (α - α ; 5); S5b - S5b : (-)-caracurine II (α - α ; 5). -

S. aenea A.W. Hill (see *S. vanprukii*). - *S. afzelii* Gilg.:

S4 - S4 : bisnor-C-alkaloid H (542), bisnor-dihydrotoxiferine (542); S5b : Wieland-Gumlich aldehyde (542); S5b - S5b : caracurine V (542). - *S. amazonica* Krukoff : C4c : (+)-macusine B (α ;543); C4f : C-mavacurine (544); S4 : ()-18-desoxy-Wieland-Gumlich aldehyde (α ;545); S4 - S4 : (-)-bisnor-dihydrotoxiferine (α - α ;545); S5b : (+)-11-methoxy-diaboline (α ;543). - *S. angolensis* Gilg.:

V4 : angustidine* (546), angustine* (546). - *S. angustiflora* Benth. (= *S. angustifolia* Benth.) : V4 : angustidine* (547), angustine* (547), angustoline* (547). - *S. axillaris* Colebr. (see *S. psilosperma*). - *S. bakanko* Bourquelot et Hérissé (see *S. madagascariensis*). - *S. borneensis* Leenhouts : V4 : angustidine* (546), angustine* (546), angustoline* (546). - *S. brachiata* Ruiz et Pavon : S5b : (+)-11-methoxy-diaboline (α ;543), (-)-Wieland-Gumlich aldehyde (α ;543). - *S. brasiliensis* (Spreng.) Mart. : S5d : (+)-strychnosilidine (α ;548), (+)-strychnosiline (α ;548); S5e : (-)-12-hydroxy-11-methoxy-spermostrychnine (α ;548), (+)-spermostrychnine (α ;548); S6b : (+)-10,11-dimethoxy-strychnobrasiline (α ;548), (-)-12-hydroxy-11-methoxy-strychnobrasiline (α ;548), (+)-strychnobrasiline (α ;548). - *S. burtoni* Bak. (see *S. madagascariensis*). - *S. camptoneura* Gilg et Busse : C3b : akagerine (549); C4a : alstonine (550), serpentine (550); D4d : (+)-camptoneurine (551); S4 : retuline (549), ()-retuline-N-oxide (α ;551); V3 : (+)-antirrhine (α ;546,552), (+)-anthirine-methosalt (α ;546,552); V4 : angustine* (546). - *S. castelneana* Wedd. : S4 - S4 : C-alkaloid D (553); S5b : diaboline (553), jobertine (553). - *S. chlorantha* Prog. : S5b : O-acetyl-diaboline (554), diaboline (554). - *S. cinnamomifolia* Thwaites (see *S. wallichiana*). - *S. colubrina* L. (see *S. wallichiana*). - *S. cuspidata* A. W. Hill (see *S. ignatii* Berg.). - *S. dale*

De Wild. : C3b : akagerine (555), kribine (555),
 17-O-methyl-akagerine (555), (-)-21-O-methyl-
 kribine (555), (-)-epi-21-O-methyl-kribine (555). -
S. decussata (Pappe) Gilg : V4 : (-)-gluco-alkaloid
 (556). - *S. dewevrei* Gilg (see *S. icaja*). - *S. diaboli*
 Sandwith : S5b : (+)-diaboline (α ;557). - *S. divaricans*
 Ducke : C4f : C-mavacurine (558); S4 : C-fluorocurarine
 (558); S4 - S4 : C-calebassine (558), C-curarine I (558). -
S. dolichothyrsa Gilg ex Onochie et Hepper: S4 : 18-
 desoxy-Wieland-Gumlich aldehyde (559); S4 - S4 : bisnor-
 C-alkaloid D (559), bisnor-C-curarine (559), bisnor-
 dihydrotoxiferine (559), bisnor-dihydrotoxiferine-di-N-
 oxide (559), bisnor-dihydrotoxiferine-N-oxide (559);
S5b - S5b : caracurine V (560), caracurine-V-di-N-oxide
 (560), caracurine-V-N-oxide(560). - *S. dysophylla* Benth.
 (see *S. madagascariensis*). - *S. elaeocarpa* Gilg ex Leeuwen-
 berg : C3b : akagerine (555), kribine (555), 17-O-methyl-
 akagerine (555), (-)-21-O-methyl-kribine (555), (-)-epi-
 21-O-methyl-kribine (555). - *S. fendleri* (Sprague et Sand-
 with) : S5e : (+)-N_a-acetyl-strychnosplendine (α ;561),
 (-)-12-hydroxy-11-methoxy-N_a-acetyl-strychnosplendine (α ;
 561); S6b : (-)-12-hydroxy-11-methoxy-strychnofendlerine
 (α ;561), (+)-strychnofendlerine (α ;561). - *S. floribunda*
 Gilg : V4 : angustine* (546). - *S. froesii* Ducke : C4f :
 C-mavacurine (562); S4 : ()-18-desoxy-Wieland-Gumlich

aldehyde (α ;545); S4 - S4 : C-alkaloid E (563),
 C-curarine I (563), C-dihydrotoxiferine (563), C-toxi-
 ferine I (563); S5b : diaboline (545), Wieland-Gumlich
 aldehyde (545). - *S. gauthieriana* Pierre (see *S. walli-*
chiana). - *S. gossweileri* Exell : C3a : ()-diploceline
 (α ;564); C4a : alstonine (565); D3a : ()-dolichanthoside
 (α ;566). - *S. heterodoxa* Gilg (see *S. potatorum*). - *S.*
holstii forma *condensata* Duvign. (= *S. henningsii* Gilg;
 = *S. holstii* Gilg var. *reticulata* (Burt-Davy et Honoré)
 Duvign. forma *condensata* Duvign., *S. procera* Gilg et Busse,
S. reticulata Burt-Davy et Honoré) : S4 : N_(a)-desacetyl-
 17-O-acetyl-18-hydroxy-isoretuline (567), N_(a)-desacetyl-
 18-hydroxy-isoretuline (567), N_(a)-desacetyl-isoretuline
 (567), 18-hydroxy-isoretuline (567), (+)-retuline (α ; 567,568,
 569), tsilanimbine (567); S5b : (-)-O-acetyl-diaboline
 (α ;570), (-)-O-acetyl-henningsoline (α ;571), 2,16-dehydro-
 diaboline (572), (+)-diaboline (α ;571,572), (-)-henningsoline
 (α ;571), 11-methoxy-2,16-dehydro-diaboline (572), 11-methoxy-
 diaboline (572), (-)-11-methoxy-henningsamine (571), Wieland-
 Gumlich aldehyde (562); S5c : O-demethyl-tsilanine (567,572),
 10-methoxy-O-demethyl-tsilanine (567,572), (+)-10-methoxy-
 tsilanine (567, 572), (+)-tsilanine (α ;567,572); S6c : (+)-
 holstine (573), (+)-holstiline (573), (+)-rindline (571,
 573,574). - *S. icaia* Baill. (= *S. dewevrei* Gilg, *S. kipapa*
 Gilg) : S6a : brucine (5a), (-)-12-hydroxy-strychnine (575),

(-)-3-methoxy-strychnine (α ;576), (-)-strychnine (α ; 575); S7 : 19,20- α -epoxy-11,12-dimethoxy-N-methyl-sec-pseudostrychnine (577), (+)-19,20- α -epoxy-15-hydroxy-10,11-dimethoxy-N-methyl-sec-pseudostrychnine (α ; 576,577), (+)-19,20- α -epoxy-15-hydroxy-N-methyl-sec-pseudostrychnine (α ; 576), 19,20- α -epoxy-15-hydroxy-12-methoxy-N-methyl-sec-pseudostrychnine (577), (+)-19,20- α -epoxy-15-hydroxy-vomicine (α ; 576,577), 19,20- α -epoxy-12-methoxy-N-methyl-sec-pseudostrychnine (577), (+)-19,20- α -epoxy-11-methoxy-vomicine (α ; 576,577), 19,20- α -epoxy-N-methyl-sec-pseudo- β -colubrine (576), (+)-19,20- α -epoxy-novacine (α ;577,578), (+)-19,20- α -epoxy-vomicine (α ;576,577), (-)-15-hydroxy-icajine (α ; 576), (-)-icajine (α ;577,579), 2- or 3-methoxy-N-methyl-sec-pseudostrychnine (577), novacine (577), pseudostrychnine (580), (+)-vomicine (α ;577,579). - *S. ignatii* Berg. (= *S. cuspidata* A.W.Hill, *S.* KL 1929, *S. lanceolaris* Miq., *S. ovalifolia* Wall. ex G. Don, *S. tieuté* Lesch.) : S5b : diaboline (580), Wieland-Gumlich aldehyde (562); S6a : brucine (581), brucine-N-oxide (581), α -colubrine (582), β -colubrine (582), 12-hydroxy-strychnine (582), strychnine (581), strychnine-N-oxide (581); S7 : N-cyano-sec-pseudocolubrine (583), N-cyano-sec-pseudostrychnine (583), icajine (582), novacine (582), pseudobrucine (581), pseudostrychnine (581), vomicine (582). - *S. javanica* Hardy (see

S. walllichiana). - *S. jobertiana* Baill. : S5b : O-acetyl-diaboline (584), diaboline (584), jobertine (584). - *S. kipapa* Gilg (see *S. icaja* Baill.). - *S.* Kl 1929 (see *S. ignatii*). - *S. lanceolaris* Miq. (see *S. ignatii*). - *S. ledermannii* Gilg et Bened. : S5b : O-acetyl-diaboline (582), (+)-diaboline (α ; 585); V4 : angustine* (546). - *S. ligustrina* Blume (see *S. lucida*). - *S. lucida* R. Br. (= *S. ligustrina* Blume): C4c: normacusine B (582), sarpagine (582); S5b : diaboline (582); S6a : brucine (580), brucine-N-oxide (582), α -colubrine (582), β -colubrine (586), strychnine (580), strychnine-N-oxide (582); S7 : icajine (582), novacine (582), pseudobrucine (582). - *S. macrophylla* Barb. R. : C4f : C-mavacurine (587); C5k : C-fluorocurine (587). - *S. madagascariensis* Poir. (= *S. bakanko* Bourquelot et Hérissé, *S. burtoni* Bak., *S. dysophylla* Benth., *S. quaqua* Gilg, *S. vacacoua* Baill., *S. wakefieldii* Bak.) : S6a : strychnine (26). - *S. maingayi* C.B. Clarke : S6a : brucine (582), strychnine (582); S7 : icajine (582), vomicine (582). - *S. malaccensis* Benth. (see *S. gauthierana*). - *S. malacoclados* C.H. Wright : S5b : 11-methoxy-diaboline (550). - *S. medeola* Sagot ex Prog.: C4c : (+)-normacusine B (α ; 588); S5b : 11-methoxy-diaboline (588). - *S. melinoniana* Baill.: C4a : (-)-melinonine B (589), (-)-melinonine A (α ; 590); C4b : melinonine E (591); C4f : (+)-C-mavacurine (α ; 591); C5k : (+)-C-fluorocurine (α ; 591). - *S. minor* Dennst.:

S5b : O-acetyl-diaboline (582), diaboline (582), methoxy-diaboline (582); S6a : brucine (582), brucine-N-oxide (582), strychnine (582), strychnine-N-oxide (582); S7 : novacine (582); V4 : angustidine* (546), angustine* (546), angustoline* (546). - *S. mitscherlichii* Rich. Schomb. : C4f : C-mavacurine (558); C5k : C-fluorocurine (558); S4 : C-fluorocurarine (558); S4 - S4 : C-alkaloid D (558), C-calebassine (558), C-curarine I (558). - *S. nux-blanda* A.W. Hill : S5b : diaboline (582); S6a : brucine (582), brucine-N-oxide (582), strychnine (582), strychnine-N-oxide (582); S7 : icajine (582), novacine (582), pseudo-brucine (582), pseudostrychnine (582), vomicine (582). - *S. nux-vomica* L. : A4a : condylocarpine (592); C3a : decarbomethoxy-geissoschizine (592), geissoschizal (592), geissoschizine (592); C4c : normacusine B (592); C4f : (+)-C-mavacurine (α ;593); S5b : diaboline (582), Wieland-Gumlich aldehyde (592); S5f : isostrychnine (594); S6a : (-)-brucine (α ;593,595), brucine-N-oxide (596), (-)- α -colubrine (α ;580,597), (-)- β -colubrine (α ; 596,597), 12-hydroxy-strychnine (596), (-)-15-hydroxy-strychnine (α ; 598), (-)-strychnine (α ;593,595), strychnine-N-oxide (596); S7 : (-)-icajine (α ; 595, 596), N-methyl-sec-pseudo- β -colubrine (596), (-)-novacine (α ; 595,596), pseudobrucine (599), pseudo- α -colubrine (580,594),

pseudo- β -colubrine (580,594), (-)-pseudostrychnine (α ; 596,597), (+)-vomisine (α ; 593,595,600). - *S. odorata* A. Chev.: V4 : angustidine* (546), angustine* (546), angustoline* (546). - *S. oleifolia* A.W. Hill : S5b : O-acetyl-diaboline (582), diaboline (582). - *S. ovalifolia* Wall. ex G. Don (see *S. ignatii*). - *S. ovata* A.W. Hill : S6a : brucine (582), strychnine (582); V4 : angustidine* (546), angustine * (546), angustoline* (546). - *S. panamensis* Seem. : S4 : C-fluorocurarine (562); S4 - S4 : C-alkaloid F (562), C-alkaloid G (562), C-dihydro-toxiferine (562); S5b : diaboline (562); S6a : brucine (562), strychnine (562). - *S. parvifolia* A. DC. : C4f : C-mavacurine (562). - *S. pierriana* A.W. Hill (see *S. gauthierana*). - *S. potatorum* L.f. (= *S. heterodoxa* Gilg, *S. stuhlmannii* Gilg) : S5b : diaboline (601); S6a : brucine (582), strychnine (582); S7 : icajine (582), novacine (582); V4 : angustine* (546). - *S. pseudoquina* A.St. Hill : S4 - S4 : (-)-nordihydro-toxiferine (α ;602). - *S. psilosperma* F.v. Müll. (= *S. axillaris* Colebr.) : S5e : (-)-desacetyl-strychnospermine (α ;580), (+)-spermostrychnine (α ; 603), (+)-strychnospermine (α ;603). - *S. quadrangularis* A.W.Hill (see *S. vanprukii*). - *S. quaqua* Gilg (see *S. madagascariensis*). - *S. rheedii* C.B. Clarke (see *S. wallichiana*). - *S. romeu-belenii* Krukoff et Barneby : S5b : (+)-11-methoxy-diaboline (α ; 588, 604). - *S. rondeletiioides* Spruce : S5b : diaboline (584),

Wieland-Gumlich aldehyde (584). - *S. rubiginosa* A.DC. : S4 : C-fluorocurarine (563); S4 - S4 : C-calebassine (563). - *S. rupicola* Pierre ex Dop : S6a : brucine (582), brucine-N-oxide (582), strychnine (582); S7 : icajine (582), N-methyl-sec-pseudobrucine (582), N-methyl-sec-pseudostrychnine (582), novacine (582), pseudobrucine (582); V4 : angustidine* (582), angustine* (582), angustoline* (582). - *S. samba* Duvign. : V4 : angustidine* (546), angustine* (546), angustoline* (546). - *S. scheffleri* Gilg (= *S. subaquatica* De Wild.; *S. volubilis* Duvign. ex Denöel) : V4 : angustidine* (546), angustine * (546), angustoline* (546). - *S. solerederi* Gilg : S5b : diaboline (562). - *S. solimoesana* Krukoff : S4 : C-fluorocurarine (605); S4 - S4 : C-alkaloid D (605), C-alkaloid E (605), C-alkaloid F (605), C-alkaloid G (605), C-calebassine (605), C-curarine I (605). - *S. splendens* Gilg : S5e : (+)-N_a-acetyl-isostrychnosplendine (α; 603,606,607), (+)-isosplendoline (α; 603,606,607), (-)-isostrychnosplendine (α; 603,606,607), (+)-splendoline (α; 603,606), (-)-strychnosplendine (α; 603,606,607); S6b : (+)-iso-splendine (α; 603,607). - *S. stuhlmannii* Gilg (see *S. potatorum*). - *S. subaquatica* De Wild (see *S. scheffleri*). - *S. subcordata* Spruce : C4f : C-mavacurine (608); C5k : C-fluorocurine (608); S4 : C-fluorocurarine (608); S5b : Wieland-Gumlich aldehyde (608). - *S. tabascana* Sprague et

Sandwith : S5d : (+)-strychnosilidine (α ;609), ()-tabascanine (α ;609); S6b : ()-10-methoxy-strychnobrasililene (α ;609), ()-N_a-acetyl-O-methyl-strychnosplendine (α ;609), (+)-strychnobrasililene (α ;609). - *S. tieuté* Lesch. (see *S. ignatii*). - *S. tomentosa* Benth. : S4 : C-fluorocurarine (610); S4 - S4 : C-alkaloid E (610), C-toxiferine I (610). - *S. toxifera* Schomb.: C4c : (-)-macusine A (α ;611), (+)-macusine B (α ;611), (-)-macusine C (α ;540); C4f : (+)-C-mavacurine (α ;612), C-profluorocurine (612); C5k : (+)-C-fluorocurine (α ;612); S4 - S4 : C-alkaloid A (611), (-)-nordihydrotoxiferine (α ;613), (-)-C-toxiferine I (α ;611); S5b : (-)-Wieland-Gumlich aldehyde (α ;611), (-)-N_b-Wieland-Gumlich aldehyde-chlormethylate (α ;611); S5b - S5b : (-)-caracurine II (α - α ;614), (-)-caracurine-II-methosalt (α - α ;615), (+)-caracurine V (α - α ; 612). - *S. trichoneura* Leeuwenberg : V4 : angustidine* (546), angustine* (546), angustoline* (546). - *S. trinervis* (Vell.) Mart. : S4 : C-fluorocurarine (616); S4 - S4 : C-alkaloid H (616), C-calebassine (616), C-curarine I (616), C-dihydrotoxiferine (616). - *S. tschibangensis* Pellegr. : C3a : (+)-tschibagensine (α ;617). - *S. umbellata* (Lour.) Merr. : S5b : diaboline (582); S6a : brucine (582), strychnine (582); S7 : icajine (582); V4 : angustidine* (546), angustine* (546), angustoline* (546). - *S. urceolata* Leeuwenberg :

S4 - S4 : bisnor-C-alkaloid H (618), bisnor-dihydro-toxiferine (618); S5b - S5b : caracurine V (618). - *S. usambarensis* Gilg (= *S. fernandiae* Duvign. ex Denöel; *S. menyanthoides* Duvign. ex Denöel; *S. micans* Duvign. ex Denöel) : C3a : 3',4'-dihydro-usambarensine (619, 620), ()-18,19-dihydro-usambaridine Br (α ;621), ()-18,19-dihydro-usambaridine Vi (α ;621), 18,19-dihydro-usambarine (621), N' _(b)-methyl-3',4'-dihydro-usambarensine (622), ()-isostrychnopentamine A (α ;621), ()-isostrychnopentamine B (α ;621), N' _(b)-methyl-usambarensine (622), ()-strychnobaridine (α ;621), ()-strychnopentamine (α ; 621, 623), ()-usambarensine (α ; 619,622), usambaridine (624), ()-usambaridine Br (α ;621), ()-usambaridine Vi (α ;621), ()-usambarine (α ; 620,621,624,625); C3b : ()-akagerine (α ; 626); C4b : decarbomethoxy-dihydro-gambirtannine (627); C4c : macusine B (628), O-methyl-dihydro-macusine B (628), O-methyl-macusine B (628); C4d : ()-isostrychnofoline (α ;629), ()-isostrychnophylline (α ; 629), ()-strychnofoline (α ;630), ()-strychnophylline (α ; 629); S4-S4 : afrocurarine (622), C-calebassine (622), C-curarine (622),C-dihydrotoxiferine (622); V4 : angustine* (546). - *S. vacacoua* Baill. (see *S. madagascariensis*). - *S. vanprukii* Craib (= *S. aenea* A.W. Hill; *S. quadrangularis* A.W. Hill) : V4 : angustidine* (546), angustine* (546), angustoline* (546). - *S. variabilis* De Wild.: S4 : (+)-

N_a -acetyl-2,16-dihydro-2 β ,16 α -akuammicinal (α ;631),
 desacetyl-isoretuline (632), (-)-desacetyl-retuline
 (α ;633), isoretuline (632), retuline (632); S4 - S4 :
 nordihydrotoxiferine (634); S4 - S5a : 12'-hydroxy-iso-
 strychnobiline (632), isostrychnobiline (634), strychno-
 biline (634). - *S. volubilis* Duvign. ex Denöel (see
S. scheffleri). - *S. wakefieldii* Bak. (see *S. madagascariensis*). - *S. wallichiana* Steud. ex A.DC. (= *S. cinnamomifolia*
 Thwaites; *S. colubrina* L.; *S. gauthieriana* Pierre; *S. javanica* Hardy ex Rabuteau et Piétri; *S. pierriana* A.W. Hill;
S. rheedii C.B. Clarke) : S6a : brucine (635, 636), brucine-
 N-oxide (636), α -colubrine (635), β -colubrine (582), (-)-
 12-hydroxy-11-methoxy-strychnine (α ;635), 12-hydroxy-
 strychnine (635, 636), strychnine (635, 636), strychnine-
 N-oxide (636); S7 : N-cyano-sec-pseudobrucine (583, 636),
 N-cyano-sec-pseudostrychnine (583, 636), 15-hydroxy-icajine
 (636), (+)-12-hydroxy-11-methoxy-N-methyl-sec-pseudostrych-
 nine (α ;635), 12-hydroxy-11-methoxy-pseudostrychnine (582),
 15-hydroxy-novacine (636), icajine (636), icajine-N-oxide
 (636), N-methyl-sec-pseudo- β -colubrine (636), novacine (635,
 636), (-)-pseudobrucine (α ; 636,637), (-)-pseudostrychnine
 (α ; 583,636,637), vomicine (635); V4 : angustidine* (582),
 angustine* (582), angustoline* (582). - *S. xantha* Leeuwen-
 berg : V4 : angustidine* (546), angustine* (546), angusto-
 line* (546).

RUBIACEAEAdina (NAU)

A. cordifolia Hook. : D3a : cordifoline (638), (-)-10-desoxy-cordifoline (α ;639); D4g : ()-adifoline (α ;640), (+)-10-desoxy-adifoline (383). - *A. rubescens* Hemsl.: C3a : (-)-adirubine (α ; 641,642), (-)-anhydro-adirubine (α ;642); C4a : (-)-5 α -carboxy-tetrahydroalstonine (α ; 4); C4b : (-)-5 α -carboxy-corynanthine (α ;643); D3a : (-)-10-desoxy-cordifoline (α ;644), ()-5-oxo-strictosidine (α ;645), (-)-vincoside (α ;646); D4a : ()-macrolidine (α ;647); D4c : (-)-desoxy-cordifoline-lactam (648); D5c : (-)-rubenine (α ;649); V4 : (-)-10- β -D-glucosyloxy-vincoside-lactam (α ; 6), (-)-rubescine (α ;650), (-)-3 α ,5 α -tetrahydro-desoxy-cordifoline-lactam (α ;651), (-)-3 β ,5 α -tetrahydro-desoxy-cordifoline-lactam (α ;651). - *A. rubrostipulata* K. Schum. (see *Mitragyna rubrostipulata*).

Anthocephalus (NAU)

A. cadamba (Roxb.) Miq. (see *A. cinensis*). - *A. cinensis* (Lam.) Rich. (= *A. cadamba* (Roxb.) Miq.) : D3a : strictosidine (652); D4a : (-)-3 α -dihydro-cadambine (α ; 652,653), 3 β -dihydro-cadambine (652); D4b : (-)-cadamine* (654),

isocadamine (654), ()-isodihydro-cadambine (α ; 655),
 3 β -isodihydro-cadambine (652); D5a : (-)-cadambine
 (α ; 653).

Antirhea (GUE)

A. putaminosa (F.v.Müll.) Bailey : V3 : (-)-antirhine
 (α ; 656).

Cephalanthus (NAU)

C. occidentalis L. : C3a : dihydro-corinanthine (657),
 hirsutine (657); C4d : anti-isorhynchophylline-N-oxide
 (657), isorhynchophylline (657), rhynchophylline (657),
 rhynchophylline-N-oxide (657).

Cinchona (CIN)

C. calisaya var. *javanica* (see *C. officinalis*). -
C. erythrantha (see *C. pubescens*). - *C. ledgeriana* (see
C. officinalis). - *C. nitida* (see *C. officinalis*). - *C.*
officinalis L. (= *C. calisaya* Wedd. var. *javanica* Moens;
C. ledgeriana Moens; *C. nitida* R. et P.) : C4g : (+)-
 cinchophyllamine (658), (+)-isochinchophyllamine (α ; 658);
C5l : (+)-quinamine (α ; 658). - *C. pelletieriana* (see *C.*
pubescens). - *C. pubescens* Vahl. (= *C. erythrantha* Pav.;

C. pelletieriana Wedd.; *C. succirubra* Pav.) : C4a : aricine (5a); C51 : (+)-quinamine (α ;659), (+)-conquinamine (α ;660). - *C. rosulenta* Howard : C51 : (+)-quinamine (α ;659), (+)-conquinamine (α ;660). - *C. succirubra* (see *C. pubescens*).

Corynanthe (CIN)

C. macroceras (K. Schum.) Pierre (see *Pausinystalia macroceras*). - *C. mayumbensis* (R.Good) N. Hallé (= *Pseudocinchona mayumbensis* (R.Good) Ham.) : C4a : akuammigine (661), (-)-19-epi-ajmalicine (661), 3-iso-19-epi-ajmalicine (661), (+)-3-iso-rauneticine (α ;661), rauneticine (661), tetrahydroalstonine (661); C4b : (-)-corynanthine (α ; 662). - *C. pachyceras* K. Schum. (= *Pseudocinchona africana* Aug. et Chev.) : C3a : (-)-corynantheidine (α ;663), (-)-corynantheine (α ; 663,664), (+)-dihydro-corynantheine (α ; 663); C4b : (-)-corynanthine (α ;662), (-)- α -yohimbine (α ; 665), (-)- β -yohimbine (α ;665); C4d : (-)-corynoxine (α ;666), (-)-corynoxine (α ;666). - *C. paniculata* Welw. : C4b : alloyohimbine (667), pseudoyohimbine (667), yohimbine (667), β -yohimbine (667). - *C. yohimbe* K.Schum. (see *Pausinystalia yohimba*).

Guettarda (GUE)

G. eximia : C4a : (-)-cathenamine (α ;668).

Iserertia (MUS)

I. hypoleuca Benth. : C51 : (+)-18,19-dihydro-quinamine (669, 670), (-)-isodihydro-quinamine (670).

Mitragyna (NAU)

M. africana (Willd.) O. Kuntze (see *M. inermis*). - *M. ciliata* Aubr. et Pellegr. : C3a : ()-mitraciliatine (α ; 671, 672); C4d : (-)-ciliaphylline (α ; 671, 672, 673), isorhynchophylline (671, 672), isorotundifoline (671, 672), (+)-rhynchociline (α ; 671, 672, 673), rhynchophylline (671), rotundifoline (671, 672). - *M. diversifolia* (Hook. F.) Havil (see *M. rotundifolia*). - *M. hirsuta* Havil : C3a : hirsuteine (674), (+)-hirsutine (α ; 675); C4a : mitrajavine (674); C4d : (+)-isorhynchophylline (α ; 675), (-)-rhynchophylline (α ; 675); C5b : (+)-isomitraphylline (α ; 675), (-)-mitraphylline (α ; 675). - *M. inermis* (Willd.) O. Kuntze (= *M. africana* (Willd.) O. Kuntze) : C3a : ()-mitraciliatine (671, 676), speciogynine (671, 676); C4d : ciliaphylline (671), isorhynchophylline (671), ()-isorhynchophylline-N-oxide (α ; 677), isorotundifoline (671), rhynchociline (671), rhynchophylline (671), ()-rhynchophylline-N-oxide (α ; 677), rotundifoline (671); C5b : speciophylline (671), uncarine F (671). - *M. javanica* Koord. et Valeton : C4a : (-)-ajmalicine (α ; 678), (-)-mitrajavine (675, 679); C5b :

(+)-isomitraphylline (α ;675), (+)-javaphylline (α ; 678),
 (-)-mitraphylline (α ;675), (+)-vineridine (α ; 675);
V4 : angustine* (546). - *M. macrophylla* Hiern. (see *M.*
stipulosa). - *M. parvifolia* (Roxb.) Korth. : C3a :
 dihydro-corynantheine (680), hirsutine (680, 681); C4a :
 ajmalicine (682), akuammigine (680, 681), 3-isoajmalicine
 (680), tetrahydro-alstonine (682); C4d : ciliaphylline (680,
 681), isorhynchophylline (680, 681), isorotundifoline
 (683), isorotundifoline (680, 683), rhynchociline (680,
 681), rhynchophylline (680, 681), rotundifoline (683),
 rotundifoline (680); C5b : isomitraphylline (680),
 isopteropodine (680, 681), mitraphylline (680), pteropodine
 (680, 681), speciophylline (680, 681), uncarine F (680, 681);
V4 : angustine* (546). - *M. rotundifolia* (Roxb.) O.Kuntze
 (= *M. diversifolia* (Hook.F.) Havil : C4a : 3-isoajmalicine
 (684); C4d : ciliaphylline (684), corynoxine (684), ()-
 isocorynoxine (α ;684), isorhynchophylline (684), ()-iso-
 rhynchophylline-N-oxide (α ;677), rhynchociline (684), (-)-
 rhynchophylline (α ; 684,685), ()-rhynchophylline-N-oxide (α ; 677), (+)-
 rotundifoline (α ;685); C5b: isomitraphylline (684), mitraphylline(684).- *M.*
rubrostipulaceae Havil (see *M. rubrostipulata*). - *M. rubrosti-*
pulata (K.Schum.) Havil (= *Adina rubrostipulata* K. Schum.; *M.*
rubrostipulaceae Havil) : C3a : hirsutine (686), hirsutine
 (686); C4d : ()-anti-rotundifoline-N-oxide (α ; 686,687),
 isorhynchophylline (686), isorotundifoline (686), rhyncho-

phylline (686), rhynchophylline-N-oxide (686), rotundifoline (686); C5b : isomitraphylline (686), (-)-mitraphylline (α ; 686). - *M. speciosa* Korth. : C3a : (-)-corynantheidine (α ; 688), isocorynantheidine (689), isopaynantheine (689), mitraciliatine (689), (-)-mitragynine (α ; 690), (-)-paynantheine (α ; 688, 690), (-)-speciociliatine (α ; 690), (+)-speciogynine (α ; 688, 690); C4a : (-)-ajmalicine (α ; 688, 690), akuammigine (689), 3-isoajmalicine (689), mitrajavine (689); C4d : ciliaphylline (689, 690), corynoxine (690), corynoxine A (690), corynoxine B (690), (-)-3-epi-isorotundifoline (α ; 683), (-)-isomitrafoline (α ; 683), isorhynchophylline (689, 690), (-)-isorotundifoline (α ; 683), (-)-isorotundifoline (α ; 683), (-)-isospeciofoline (α ; 683, 690), (-)-isospecionoxine (α ; 673), (-)-mitrafoline (α ; 683, 690), mitragynine oxindol A (690), mitragynine oxindol B (690), rhynchociline (689, 690), (-)-rhynchophylline (α ; 673, 690), (-)-rotundifoline (α ; 683), (+)-rotundifoline (α ; 691), (-)-speciofoline (α ; 683, 690), (-)-specionoxine (α ; 673); C5b : (+)-isomitraphylline (α ; 688), javaphylline (689), (-)-mitraphylline (α ; 688), (+)-speciophylline (α ; 688). - *M. stipulosa* (D.C.) O. Kuntze (= *M. macrophylla* Hiern) : C4d : (+)-isorhynchophylline (α ; 671, 692), (-)-isorotundifoline (α ; 671, 692) (-)-rhynchophylline (α ; 671, 692), (+)-

rotundifoline (α ; 671,692); C5b : isomitraphylline (5b),
 (-)-mitraphylline (α ; 671,692). - *M. tubulosa* Havil :
C4d : ciliaphylline-N-oxide (693), ()-isorhynchophylline-
 N-oxide (α ;693), rhynchociline-N-oxide (693), ()-rhyncho-
 phylline-N-oxide (α ;693).

Nauclea (NAU)

N. coadunata (Roxb. ex J.E. Smith) Druce (see *Sarcocephalus coadunata*). - *N. diderrichii* (De Wild.) Merr. : D4a : 3 α -
 dihydro-cadambine (694, 695); D5a : cadambine (695); D6a :
 α -naucleonidine (695, 696), β -naucleonidine (695, 696), α -
 naucleonine (695, 696), β -naucleonine (695, 696). - *N. lati-*
folia Smith (see *Sarcocephalus esculentus*). - *N. parva* (Havil)
 Merr. (= *Sarcocephalus parvus*) : V4 : parvine* (697).

Neonauclea (NAU)

N. schlechteri (Val.) Merr. et Perry : C3a : (+)-gambirine
 (α ;698).

Ourouparia (NAU)

O. africana (G.Don.) Baill. (see *Uncaria africana* ssp.
africana). - *O. gambir* Baill. (see *Uncaria gambir*).

Palicourea (PSY)

P. alpina (Sw.) A.DC. : D3a : (-)-palinine (699).

Pauridiantha (URO)

P. callicarpoides (Hiern) Bremek. : D3b : pauridianthe* (700); D4e : pauridianthinine* (700). - *P. lyalli* Bremek.: D3a : (-)-lyaloside (701), (-)-pauridianthoside (702); D3b : 19-hydroxy-lyalidine (703), (+)-lyadine (704), (O)-lyalidine (703), (+)-lyaline (704), pauridianthanol (705).

Pausinystalia (CIN)

P. angolensis Wernham : C4b : alloyohimbine (667), corynanthine (667), pseudoyohimbine (667), yohimbine (667), β -yohimbine (667). - *P. macroceras* (K.Schum.) Pierre (= *Corynanthe macroceras* (K. Schum.) Pierre) : C4b : yohimbine (5a). - *P. yohimbe* (K. Schum.) Pierre (= *Corynanthe yohimbe* K. Schum.) : C3a : (+)-corynantheine (α ;706); (+)-dihydro-corynantheine (α ;706), (-)-dihydro-sitsirikine (α ; 142); C4a : (-)-ajmalicine (α ; 667,707); C4b : (-)-alloyohimbine (α ; 667,707), corynanthine (667), pseudoyohimbine (667), yohimbine (667), (-)- α -yohimbine (α ; 667,707), (-)- β -yohimbine (α ; 707).

Pseudocinchona (CIN)

P. africana Aug. et Chev. (see *Corynanthe pachyceras*). -

P. mayumbensis (Good) Ham. (see *Corynanthe mayumbensis*).

Remijia (CIN)

R. purdieana Wedd. : C4g : (+)-cinchonamine (α ;708).

Sarcocephalus (NAU)

S. coadunata (Roxb. ex. J.E. Smith) Druce (= *Nauclea coadunata* Roxb. ex J.E. Smith) : V4 : angustine* (546). -

S. esculentus Afzel (= *Nauclea latifolia* Smith) : D4a : decarbomethoxy-nauclechine* (709), naufoline* (709); V4 : angustoline* (710), angustine* (710), nauclefine (710), naucletine (710), strictosamide (711), (-)-strictosidine-lactam (α ;712). - *S. parvus* (see *Nauclea parva*).

Uncaria (NAU)

U. acida Hook. F. et Thoms. (see *U. elliptica*). - *U. acida* (Hunt.) Roxb. (see *U. acida* var. *acida*). - *U. acida* (Hunt.) Roxb. var. *acida* (= *U. acida* (Hunt.) Roxb.; *U. firma* Val.; *U. ovalifolia* Roxb.) : C4d : isorhynchophylline (713), rhynchophylline (713), rhynchophylline-N-oxide (713). -

U. acida (Hunt.) Roxb. var. *papua* Val.: C4a : 3-iso-ajmalicine (713); C4d : corynoxine (713), isorhynchophylline (713), isorhynchophylline-N-oxide (713), rhynchophylline (713), rhynchophylline-N-oxide (713). - *U. aculeata* Willd. (see *U. guianensis*). - *U. africana* G. Don. (see *U. africana* ssp. *africana*). - *U. africana* G. Don. ssp. *africana* (= *U. africana* G. Don.; *Ouroparia africana* (G. Don.) Baill.): C3a : dihydro-corynantheine (713); C4a : ajmalicine (713), 19-epi-ajmalicine (713), 3-isoajmalicine (713), 3-iso-19-epi-ajmalicine (713), tetrahydro-alstonine (713); C4b: ourouparine* (714); C4d : isorhynchophylline (713), (-)-rhynchophylline (α ; 5a, 713); C5b : isomitraphylline (713), mitraphylline (713), mitraphylline-N-oxide (713); C5t : dihydro-corynantheine-pseudoindoxyl (713). - *U. africana* G. Don. ssp. *angolensis* Welw. (= *U. angolensis* Welw.) : C4d : isorhynchophylline (713), isorhynchophylline-N-oxide (713), rhynchophylline (713), rhynchophylline-N-oxide (713). - *U. angolensis* Welw. (see *U. africana* ssp. *angolensis*). - *U. appendiculata* Benth. (see *U. lanosa* var. *appendiculata* forma *appendiculata*). - *U. attenuata* Korth. (= *U. attenuata* Korth. ssp. *attenuata* Korth.; *U. attenuata* Korth. ssp. *bulusanensis* (Elm.) Ridsd.; *U. bulusanensis* Elm.; *U. canescens* F. Vill.; *U. gambir* Wall.; *U. sclerophylla* A. DC.): C3a : dihydro-corynantheine (715), epiallo-corynantheine (715), hirsuteine (715), hirsutine (715); C4a: akuammigine (715),

3-isoajmalicine (715), 3-iso-19-epi-ajmalicine (715);
C4b : pseudoyohimbine (715); C4d : corynoxine (715),
 corynoxine B (715), isocorynoxine (715), isorhyncho-
 phylline (715), isorhynchophylline-N-oxide (715), iso-
 rotundifoline (715), rhynchophylline (715), rhyncho-
 phylline-N-oxide (715), rotundifoline (715), specio-
 foline (715); C5b : formosanine (715), isoformosanine
 (715), isomitraphylline (715), isomitraphylline-N-oxide
 (715), mitraphylline (715), mitraphylline-N-oxide (715),
 speciophylline (715); C5t : dihydro-corynantheine-pseudo-
 indoxyl (715). - *U. attenuata* Korth. ssp. *attenuata* Korth.
 (see *U. attenuata*). - *U. attenuata* Korth. ssp. *bulusanensis*
 (Elm.) Ridsd. (see *U. attenuata*). - *U. avenia* Val. (see
U. callophylla). - *U. bernaysii* F.v.Müll. (= *U. bernaysioides*
 Merr. et Perry; *U. salomonensis* (Rech.) Merr. et Perry;
U. sclerophylla Warb.) : C4a : ajmalicine (713), akuammigine
 (713, 716), 3-isoajmalicine (713), tetrahydroalstonine
 (716); C4d : isorhynchophylline (713), isorhynchophylline-
 N-oxide (713), rhynchophylline (713), rhynchophylline-N-oxide
 (713); C5b : isomitraphylline (713), (-)-isopteropodine (α ;
 717), ()-isopteropodine-N-oxide (α ; 716), mitraphylline (713),
 (-)-pteropodine (α ; 717, 718), ()-pteropodine-N-oxide (α ; 716),
 (+)-speciophylline (α ; 717, 718), ()-speciophylline-N-oxide

(α ;716), (+)-uncarine F (α ;717), ()-uncarine-F -N-oxide (α ;716); V4 : angustine* (546). - *U. bernaysioides* Merr. et Perry (see *U. bernaysii*). - *U. brevicarpa* Elm. (see *U. roxburghiana*). - *U. brevispina* Maing. ex Hook. F. (see *U. elliptica*). - *U. bulusanensis* Elm. (see *U. attenuata*). - *U. callophylla* Bl. ex Korth. (= *U. avenia* Val.; *U. jasminiflora* Hook. F.; *U. luzoniensis* Merr., *U. wrayii* King) : C3a : dihydro-corynantheine (713), gambirine (719); C4d : isorhynchophylline (713), isorotundifoline (713), rhynchophylline (713), rotundifoline (713); C5b : isomitraphylline (713), mitraphylline (713). - *U. canescens* F. Vill. (see *U. attenuata*). - *U. canescens* Korth. ssp. *velutina* (Havil.) Ridsd. (see *U. velutina*). - *U. celebica* Koord. (see *U. lanosa* var. *appendiculata* forma *philippinensis*). - *U. cirrhiiflora* Roxb. (see *U. cordata* var. *cordata* forma *cordata*). - *U. clavi-sepala* Elm. (see *U. velutina*). - *U. cordata* (Lour.) Merr. (see *U. cordata* var. *cordata* forma *cordata*). - *U. cordata* (Lour.) Merr. var. *cordata* forma *cordata* (= *U. cirrhiiflora* Roxb.; *U. cordata* (Lour.) Merr.; *U. eumececarpa* Korth.; *U. ferruginea* Kurz; *U. intermedia* Val.; *U. multiflora* Laut. et K. Schum.; *U. nemorosa* Korth.; *U. pedicellata* Roxb.; *U. sclerophylla* (Hunt.) Roxb.; *U. sclerophylla* Wall.; *U. speciosa* (Wall.)) : C4d : corynoxine A (713), corynoxine B (713), isorhynchophylline (713), rhynchophylline (713). - *U. cordata* (Lour.) Merr. var. *ferruginea* (Bl.) Ridsd. forma *ferruginea* (Bl.) Ridsd. (= *U. ferruginea* Kurz.; *U. glaucescens*

Craib.) : C3a : dihydro-corynantheine (713).- *U. cordata* (Lour.) Merr. var. *ferruginea* (Bl.) Ridsd. forma *insignis* (Bart. in DC.) Ridsd. (= *U. hallii* Korth.; *U. insignis* (Bart. in DC.); *U. sclerophylla* F. Vill.; *U. wallichii* Korth.):

C3a : dihydro-corynantheine (713); C4d : isorhynchophylline (713), rhynchophylline (713). - *U. donisii* Petit : C5b : isopteropodine (713), isopteropodine-N-oxide (713), pteropodine (713), pteropodine-N-oxide (713), specio-phylline (713), speciophylline-N-oxide (713), uncarine F (713), uncarine-F-N-oxide (713). - *U. dasycarpa* Pierre msc. (see *U. laevigata*). - *U. dasyoneura* Korth. (see *U. elliptica*). - *U. dasyoneura* Korth. var. *thwaitesii* Hook. F. (see *U. elliptica*). - *U. elliptica* R.Br. ex G.Don. (= *U. acida* Hook.F.et Thoms.; *U. brevispina* Mainq. ex Hook.F.; *U. dasyoneura* Korth.; *U. dasyoneura* Korth. var. *thwaitesii* Hook. F.; *U. gambir* Thw.; *U. rostrata* Pierre ex Pitard; *U. salaccensis* Bakh. forma nom provis.; *U. thwaitesii* Alston) : C3a : dihydro-corynantheine (713), gambirine (713); C4a : akuammigine (713), 3-isoajmalicine (713), roxburghine A (720), roxburghine B (720), roxburghine C (713, 720), roxburghine D (713, 720), roxburghine E (713, 720); C4d : isorhynchophylline (713), isorotundifoline (713), rhynchophylline (713), rotundifoline (713). - *U. eumececarpa* Korth. (see *U. cordata* var. *cordata* forma *cordata*). - *U. ferrea* f. Vill. (see *U. perrottetii*). - *U. ferrea* ssp. *appendiculata* Val. (see *U. lanson* var. *appendiculata* forma *appendiculata*).-

U. ferrea (Bl.) A.DC. (see *U. lanosa* var. *ferrea* forma *ferrea*). - *U. ferruginea* Kurz. (see *U. cordata* var. *cordata* forma *cordata*). - *U. ferruginea* Kurz. (see *U. cordata* var. *ferruginea* forma *ferruginea*). - *U. firma* Val. (see *U. acida* var. *acida*). - *U. florida* Henry (see *U. lanosa* var. *appendiculata* forma *philippinensis*). - *U. florida* Vidal (see *U. lanosa* var. *appendiculata* forma *setiloba*). - *U. formosana* (Matsum.) Hayata (see *U. hirsuta*). - *U. gambir* (Hunt.) Roxb. (= *Ouroparia gambir* Baill.) : C3a : (+)-dihydro-corynantheine (α ; 721,722), (+)-gambirine (α ;721,723a); C4a : (-)-4R-akuammigine-N-oxide (α ;724), (-)-4S-akuammigine-N-oxide (α ; 749), (-)-roxburghine A (722), (-)-roxburghine B (α ;722,725), (-)-roxburghine C (α ; 722,725), (+)-roxburghine D (α ; 722,725), (-)-roxburghine E (α ; 722,725), (-)-tetrahydro-alstonine (α ;722), (+)-4R-tetrahydro-alstonine-N-oxide (α ;724); C4b : (-)-dihydro-gambirtannine* (723b), gambirtannine* (723b), 11-methoxy-yohimbine (5a), neoxy-gambirtannine* (723b), oxo-gambirtannine* (723b), ourouparine * (726); C4d : iso-rhynchophylline (721), rhynchophylline (721), rotundifoline (721); C5b : formosanine (713), (+)-gambirdine (727), iso-formosanine (713), (+)-isogambiridine (727), (-)-mitraphylline (α ;727). - *U. gambir* Thw. (see *U. elliptica*). - *U. gambir* Wall. (see *U. attenuata*). - *U. glabrata* (Bl.)A.DC. (see *U. lanosa* var. *glabrata*). - *U. glabrata* F. Vill. (see *U. lanosa* var. *appendiculata* forma *philippinensis*). - *U. glabrescens* Merr. et Perry (see *U. lanosa* var. *appendiculata*

forma *glabrescens*). - *U. glaucescens* Craib. (see *U. cordata* var. *ferruginea* forma *ferruginea*). - *U. guianensis* (Aubl.) Gmel. (= *U. aculeata* Willd.; *U. spinosa* Raensch) : C3a : dihydro-corynantheine (713), hirsuteine (713), hirsutine (713); C4d : isorhynchophylline (713), isorhynchophylline-N-oxide (713), rhynchophylline (713), rhynchophylline-N-oxide (713); C5b : isomitraphylline (713), isomitraphylline-N-oxide (713), mitraphylline (713), mitraphylline-N-oxide (713); V4 : angustine* (546), angustoline* (713). - *U. hallii* Korth. (see *U. cordata* var. *ferruginea* forma *insignis*). - *U. havilandiana* S. Moore (see *U. longiflora* var. *longiflora*). - *U. hirsuta* Havil. (= *U. formosana* (Matsum.) Hayata; *U. uraiensis* Hayata) : C4a : 3-isoajmalicine (713); C5b : (+)-formosanine (α ; 5a, 713), isoformosanine (713), isomitraphylline (713), isomitraphylline-N-oxide (713), mitraphylline (713), mitraphylline-N-oxide (713). - *U. homomalla* Miq. (= *U. lanosa* var. *parviflora* Ridl.; *U. parviflora* Ridl.; *U. quadrangularis* Geddes; *U. tonkinensis* Havil.): C4a : 3-isoajmalicine (713); C5b : isomitraphylline (713), isomitraphylline-N-oxide (713), isopteropodine (713, 728), isopteropodine-N-oxide (713), mitraphylline (713), mitraphylline-N-oxide (713), pteropodine (713, 728), pteropodine-N-oxide (713), speciophylline (713, 728), speciophylline-N-oxide (713), uncarine F (713, 728), uncarine-F-N-oxide (713); V4 : angustidine* (546), angustine* (546), angustoline*

(546). - *U. hookeri* Val. (see *U. perrottetii*). - *U. horsfieldiana* Miq. (see *U. lanosa* var. *ferrea* forma *ferrea*). - *U. inermis* Val. (see *U. nervosa*). - *U. insignis* Bart. in DC. (see *U. cordata* var. *ferruginea* forma *insignis*). - *U. intermedia* Val. (see *U. cordata* var. *cordata* forma *cordata*). - *U. jasminiflora* Hook. F. (see *U. callophylla*). - *U. kawakamii* Hayata (see *U. lanosa* var. *appendiculata* forma *philippinensis*). - *U. korrensis* Kanehira (see *U. lanosa* var. *korrensis*). - *U. kunstleri* King : C3a : hirsutine (713); C4d : corynoxine A (713), corynoxine B (713), isorhynchophylline (713), isorhynchophylline-N-oxide (713). - *U. laevifolia* Elm. (see *U. longiflora* var. *pteropoda*). - *U. laevigata* Wall. (= *U. dasycarpa* Pierre msc.) : C5b : formosanine (713), isoformosanine (713), isomitraphylline (713), isomitraphylline-N-oxide (713), isopteropodine (713), mitraphylline (713), mitraphylline-N-oxide (713), speciophylline (713). - *U. lancifolia* Hutch.: C5b : isomitraphylline (713), mitraphylline (713), mitraphylline-N-oxide (713). - *U. lanosa* Wall. var. *appendiculata* (Benth.) Ridsd. forma *appendiculata* (Benth.) Ridsd. (= *U. appendiculata* Benth.; *U. ferrea* ssp. *appendiculata* Val.; *U. warburghii* Laut. et K.Schum.) : C5b : isomitraphylline (713), isomitraphylline-N-oxide (713), isopteropodine (713), isopteropodine-N-oxide (713), mitraphylline (713), pteropodine

(713), pteropodine-N-oxide (713), speciophylline (713), speciophylline-N-oxide (713), uncarine F (713), uncarine-F-N-oxide (713). - *U. lanosa* Wall. var. *appendiculata* (Benth.) Ridsd. forma *glabrescens* (Merr. et Perr.) Ridsd. (= *U. glabrescens* Merr. et Perry) : C4a : akuammigine (713); C5b : isopteropodine (713), isopteropodine-N-oxide (713), pteropodine (713), pteropodine-N-oxide (713), speciophylline (713), speciophylline-N-oxide (713), uncarine F (713), uncarine-F-N-oxide (713). - *U. lanosa* Wall. var. *appendiculata* (Benth.) Ridsd. forma *philippinensis* (Elm.) Ridsd. (= *U. celebica* Koord.; *U. florida* Henry; *U. glabrata* F. Vill.; *U. kawakami* Hayata; *U. philippinensis* Elm.; *U. setiloba* Sasaki) : C5b : (+)-formosanine (α ; 75, 729, 730), (+)-isoformosanine (α ; 75, 729, 730), isopteropodine (713), isopteropodine-N-oxide (713), (-)-mitraphylline (α ; 731), pteropodine (713), pteropodine-N-oxide (713), speciophylline (713), speciophylline-N-oxide (713), uncarine F (713), uncarine-F-N-oxide (713). - *U. lanosa* Wall. var. *appendiculata* (Benth.) Ridsd. forma *setiloba* (Benth.) Ridsd. (= *U. florida* Vidal; *U. setiloba* Benth.) : C5b : isomitraphylline (713), isomitraphylline-N-oxide (713), isopteropodine (75), isopteropodine-N-oxide (713), mitraphylline (713), mitraphylline-N-oxide (713), (-)-pteropodine (α ; 75, 729, 732), pteropodine-N-oxide (713), (+)-speciophylline (α ; 729, 732), speciophylline-N-oxide (713), uncarine F (713), uncarine-F-N-oxide (713). - *U. lanosa*

Wall. var. *ferrea* (Bl.) Ridsd. forma *ferrea* (Bl.) Ridsd.
 (= *U. ferrea* (Bl.) A.DC.; *U. horsfieldiana* Miq.) : C5b :
 isomitraphylline (713), (-)-isopteropodine (α ;717), iso-
 pteropodine-N-oxide (713), mitraphylline (713), mitra-
 phylline-N-oxide (713), (-)-pteropodine (α ;717), ptero-
 podine-N-oxide (713), (+)-speciophylline (α ;717), specio-
 phylline-N-oxide (713), (+)-uncarine F (α ;717), uncarine-
 F-N-oxide (713). - *U. lanosa* Wall. var. *glabrata* (Bl.)
 Ridsd. (= *U. glabrata* (Bl.) A.DC.; *U. lobbii* Hook. F.) :
C5b : isopteropodine (713), isopteropodine-N-oxide (713),
 pteropodine (713), pteropodine-N-oxide (713), speciophylline
 (713), speciophylline-N-oxide (713), uncarine F (713),
 uncarine-F-N-oxide (713). - *U. lanosa* Wall. var. *korrensis*
 (Kanehira) Ridsd. (= *U. korrensis* Kanehira) : C5b : iso-
 mitraphylline (713), isomitraphylline-N-oxide (713), iso-
 pteropodine (713), isopteropodine-N-oxide (713), mitra-
 phylline (713), mitraphylline-N-oxide (713), pteropodine
 (713), pteropodine-N-oxide (713), speciophylline (713),
 speciophylline-N-oxide (713), uncarine F (713), uncarine-F-
 N-oxide (713). - *U. lanosa* Wall. var. *lanosa* : C5b : iso-
 pteropodine (713), isopteropodine-N-oxide (713), pteropodine
 (713), pteropodine-N-oxide (713), speciophylline (713),
 speciophylline-N-oxide (713), uncarine F (713), uncarine-F-
 N-oxide (713). - *U. lanosa* var. *parviflora* Ridl. (see *U. homo-*
malla). - *U. lanosa* Wall. var. *toppingii* (Merr.) Ridsd. forma

toppingii (Merr.) Ridsd. (= *U. toppingii* Merr.) : C5b : isomitraphylline (713), isomitraphylline-N-oxide (713), isopteropodine (713), isopteropodine-N-oxide (713), mitraphylline (713), mitraphylline-N-oxide (713), pteropodine (713), speciophylline (713), speciophylline-N-oxide (713), uncarine F (713). - *U. lobbii* Hook. F. (see *U. lanosa* var. *glabrata*). - *U. longiflora* (Poir.) Merr. var. *longiflora* (= *U. havilandiana* S. Moore; *U. oligoneura* Korth.; *U. pachyphylla* Merr.; *U. pteropoda* Merr.; *U. trinervis* Havil) : C4d : corynoxine or corynoxine (713), corynoxine B (713), isocorynoxine (713), isorhynchophylline (713), isorhynchophylline-N-oxide (713), rhynchophylline (713), rhynchophylline-N-oxide (713); C5b : isomitraphylline (713), isomitraphylline-N-oxide (713), isopteropodine (713), isopteropodine-N-oxide (713), mitraphylline (713), mitraphylline-N-oxide (713), pteropodine (713), pteropodine-N-oxide (713), speciophylline (713), speciophylline-N-oxide (713), uncarine F (713), uncarine-F-N-oxide (713). - *U. longiflora* (Poir.) Merr. var. *pteropoda* (Miq.) Ridsd. (= *U. laevifolia* Elm.; *U. pteropoda* Miq.) : C4d : corynoxine (713), isocorynoxine (713), isorhynchophylline (713), rhynchophylline (713); C5b : isomitraphylline (733), (-)-isopteropodine (α ; 733, 734), isopteropodine-N-oxide (733), mitraphylline (733), (-)-pteropodine (α ; 733, 734), pteropodine-N-oxide (733), speciophylline (733), speciophylline-N-oxide (733), uncarine F (733). -

U. luzoniensis Merr. (see *U. callophylla*). - *U. macrophylla* Wall. (= *U. sessifolia* (Roxb. ex Spreng.) Kurz.): C4d : (-)-corynoxine A (α ;735), (-)-corynoxine B (α ;735), isorhynchophylline (735), isorhynchophylline-N-oxide (713), rhynchophylline (735), rhynchophylline-N-oxide (713). - *U. membranifolia* How. (see *U. sinensis*). - *U. multiflora* Laut. et K. Schum. (see *U. cordata* var. *cordata* forma *cordata*). - *U. nemorosa* Korth. (see *U. cordata* var. *cordata* forma *cordata*). - *U. nervosa* Elm. (= *U. inermis* Val.; *U. sclerophylloides* Val.; *U. valettoniana* Merr. et Perry) : C3a : dihydro-corynantheine (713), hirsuteine (713), hirsutine (713). - *U. oligoneura* Korth. (see *U. longiflora* var. *longiflora*). - *U. orientalis* Guill. : C4a : ajmalicine (713), akuammigine (713), 3-iso-ajmalicine (715), 3-iso-19-epi-ajmalicine (713); C5b : formosanine (713), isoformosanine (713), isomitraphylline (715), isomitraphylline-N-oxide (715), isopteropodine (715), isopteropodine-N-oxide (715), mitraphylline (715), mitraphylline-N-oxide (715), pteropodine (715), pteropodine-N-oxide (715), speciophylline (715), speciophylline-N-oxide (715), uncarine F (715), uncarine-F-N-oxide (715). - *U. ovalifolia* Roxb. (see *U. acida* var. *acida*). - *U. pachyphylla* Merr. (see *U. longiflora* var. *longiflora*). - *U. parviflora* Ridl. (see *U. homomalla*). - *U. pedicellata* Roxb. (see *U. cordata* var. *cordata* forma *cordata*). - *U. perrottetii* (A. Rich.) Merr. (= *U.*

ferrea f. Vill.; *U. hookeri* Val.) : C5b : isomitraphylline (713), isomitraphylline-N-oxide (713), isopteropodine (713), mitraphylline (713), mitraphylline-N-oxide (713), (-)-pteropodine (α ; 718), (+)-speciophylline (α ; 718), uncarine F (713). - *U. philippinensis* Elm. (see *U. lanosa* var. *appendiculata* forma *philippinensis*). - *U. pilosa* Roxb. (see *U. scandens*). - *U. pteropoda* Merr. (see *U. longiflora* var. *longiflora*). - *U. pteropoda* Miq. (see *U. longiflora* *pteropoda*). - *U. quadrangularis* Geddes (see *U. homomalla*). - *U. rhynchophylla* (Miq.) Miq. ex. Havil. (= *Ouroparia rhynchophylla* Matsum.; *U. rhynchophyllodes* How.) : C3a : corynantheine (75, 732, 736), (+)-dihydro-corynantheine (α ; 75, 732, 736), (+)-geissoschizine methylether (α ; 75, 737), (+)-hirsuteine (α ; 75, 732, 736), (+)-hirsutine (α ; 75, 732, 736); C4a : (-)-akuammigine (α ; 75, 737); C4d : (-)-corynoxine (α ; 75, 732, 736, 738), isocorynoxine (75, 732, 736), (+)-isorhynchophylline (α ; 75, 729), (-)-rhynchophylline (α ; 75, 729, 736), rhynchophylline-N-oxide (713); V4 : angustidine* (546), angustine* (546), angustoline* (546). - *U. rhynchophyllodes* How. (see *U. rhynchophylla*). - *U. rostrata* Pierre ex Pitard (see *U. elliptica*). - *U. roxburghiana* Korth. (= *U. brevicarpa* Elm.) : C5b : isopteropodine (713), isopteropodine-N-oxide (713), pteropodine (713), pteropodine-N-oxide (713), speciophylline (713), speciophylline-N-oxide (713), uncarine F (713), uncarine-F-

N-oxide (713). - *U. salaccensis* Bakh. forma nom provis.
 (see *U. elliptica*). - *U. salomonensis* (Rech.) Merr. et
 Perry (see *U. bernaysii*). - *U. scandens* (Smith.) Hutch.
 (= *U. pilosa* Roxb.; *U. wangi* How.) : C5b : isomitraphylline
 (713), isomitraphylline-N-oxide (713), isopteropodine (713),
 isopteropodine-N-oxide (713), mitraphylline (713), mitra-
 phylline-N-oxide (713), pteropodine (713), pteropodine-N-
 oxide (713), speciophylline (713), speciophylline-N-oxide
 (713), uncarine F (713). - *U. sclerophylla* A. DC. (see
U. attenuata). - *U. sclerophylla* (Hunt.) Roxb. (see *U.*
cordata var. *cordata* forma *cordata*). - *U. sclerophylla*
 F. Vill. (see *U. cordata* var. *ferruginea* forma *insignis*). -
U. sclerophylla Wall. (see *U. cordata* var. *cordata* forma
cordata). - *U. sclerophylla* Warb. (see *U. bernaysii*). -
U. sclerophylloides Val. (see *U. nervosa*). - *U. sessifolia*
 (Roxb. ex Spreng.) Kurz. (see *U. macrophylla*). - *U. sessili-*
fructus Roxb. : C3a : hirsutine (713); C4a : akuammigine
 (713), 3-isoajmalicine (713), 3-iso-19-epi-ajmalicine
 (713); C4d : corynoxine A (713), corynoxine B (713),
 isorhynchophylline (713), rhynchophylline (713); C5b :
 formosanine (713), isoformosanine (713), isomitraphylline (713),
 isomitraphylline-N-oxide (713), mitraphylline (713), mitra-
 phylline-N-oxide (713), uncarine F (713). - *U. setiloba*
 Benth. (see *U. lanosa* var. *appendiculata* forma *setiloba*). -
U. setiloba Sasaki (see *U. lanosa* var. *appendiculata* forma
philippinensis). - *U. sinensis* (Oliv.) Havil. (= *U. membrani-*

folia How.) : C4a : akuammigine (713); C5b : isopteropodine (713), isopteropodine-N-oxide (713), pteropodine (713), pteropodine-N-oxide (713), speciophylline (713), speciophylline-N-oxide (713), uncarine F (713), uncarine-F-N-oxide (713). - *U. speciosa* Wall. (see *U. cordata* var. *cordata* forma *cordata*). - *U. spinosa* Raensch (see *U. guianensis*). - *U. sterrophylla* Merr. et Perry : C4a : 3-isoajmalicine (713); C4d : isorhynchophylline (713), rhynchophylline (713); C5b : isomitraphylline (713), isopteropodine (713), mitraphylline (713), pteropodine (713), speciophylline (713), speciophylline-N-oxide (713), uncarine F (713). - *U. surinamensis* Miq. (see *U. tomentosa*). - *U. talbotii* Wernh. : C4d : isorhynchophylline (713), rhynchophylline (713). - *U. thwaitesii* Alston (see *U. elliptica*). - *U. tomentosa* A. DC. (= *Ouroparia guianensis* Aublet.; *U. surinamensis* Miq.) : C3a : dihydro-corynantheine (739), dihydro-corynantheine-N-oxide (739), hirsutine (739), hirsutine (739), hirsutine-N-oxide (739); C4d : isorhynchophylline (739), isorhynchophylline-N-oxide (739), isorotundifoline (739), (-)-rhynchophylline (α ; 739,740), rhynchophylline-N-oxide (739), rotundifoline (739); C5b : isomitraphylline (739), isomitraphylline-N-oxide (739), mitraphylline (739). - *U. tonkinensis* Havil. (see *U. homomalla*). - *U. toppingii* Merr. (see *U. lanosa* var. *toppingii* forma *toppingii*). - *U. trinervis* Havil. (see *U. longiflora* var.

longiflora). - *U. uraiensis* Hayata (see *U. hirsuta*). -
U. valettoniana Merr. et Perry (see *U. nervosa*). -
U. velutina Havil. (= *U. canescens* Korth. ssp. *velutina*
(Havil.) Ridsd.; *U. clavisepala* Elm.) : C5b : isomitra-
phylline (713), isopteropodine (715), isopteropodine-N-
oxide (715), mitraphylline (713), pteropodine (715),
pteropodine-N-oxide (715), speciophylline (715), specio-
phylline-N-oxide (715), uncarine F (715), uncarine-F-N-
oxide (715). - *U. wallichii* Korth. (see *U. cordata* var.
ferruginea forma *insignis*). - *U. wangii* How. (see *U.*
scandens). - *U. warburghii* Laut. et K.Schum. (see *U. lanosa*
var. *appendiculata* forma *appendiculata* . - *U. wrayii* King
(see *U. callophylla*).

List of synonymous alkaloid names

(The preferred version ist written in italics)

- burnamine = *desacetyl-picraline*
- caracurine VII = *Wieland-Gumlich aldehyde*
- condensamine = *11-methoxy-henningsamine*
- desacetyl-diaboline = *Wieland-Gumlich aldehyde*
- desacetyl-picraline = *burnamine*
- dimethoxy-picrinine = *quaternine*
- elegantine = *isomajdine*
- elliptamine = *reserpiline*
- 3-epi- α -yohimbine = *isorauhimbine*
- 19,20- α -epoxy-12,15-dihydroxy-N-methyl-sec-pseudostrychnine =
19,20- α -epoxy-15-hydroxy-vomicine
- 19,20- α -epoxy-15-hydroxy-novacine = *19,20- α -epoxy-15-hydroxy-*
10,11-dimethoxy-N-methyl-sec-pseudostrychnine
- grandifoline = *amataine*
- henningsamine = *O-acetyl-diaboline*
- 10-hydroxy-akuammicine = *sewarine*
- 3-hydroxy- α -colubrine = *pseudo- α -colubrine*
- 3-hydroxy- β -colubrine = *pseudo- β -colubrine*
- hydroxyindolenine-conopharyngine = *jollyanine*
- isovincoside = *striootsidine*
- kopsinoline = *kopsinine-N-oxide*
- 11-methoxy-compactinervine = *alstovine*

11-methoxy-epi-3 α -yohimbine = *quaternatine*

montanine = *voacristine-pseudoindoxyl*

reserpine-N-oxide = *renoxydine*

rhazinine = *antirrhine*

subsesseline = *amataine*

taberpsychine = *anhydro-vobasine-diol*

tombozine = *normacusine B*

uncarine A = *isoformosanine*

uncarine B = *formosanine*

uncarine C = *pteropodine*

uncarine D = *rauvoxinine*

uncarine E = *isopteropodine*

vinamidine = *catharinine*

vincamidine = *strictamine*

vincovine = *vinorine*

vincristine = *leurocristine*

voacangarine = *voacristine*

voaphylline = *conoflorine*

vomifoline = *peraksine*

List of Abbreviations

A	=	Aspidospermatan
ALS	=	Alstoniae
APO	=	Apocynaceae
C	=	Corynanthean
CAR	=	Carisseae
CIN	=	Cinchoneae
D	=	Vincosan
E	=	Eburnan
GEL	=	Gelsemieae
GUE	=	Guettardeae
J	=	Ibogan
LOG	=	Loganiaceae
MUS	=	Mussaendeae
NAU	=	Naucleaeae
P	=	Plumeran
PSY	=	Pschotrieae
RAU	=	Rauwolfieae
RUB	=	Rubiaceae
S	=	Strychnan
STR	=	Strychneae
TAB	=	Tabernaemontaneae
URO	=	Urophylleae
V	=	Vallesiachotaman

Summary

All of the indole alkaloids with a C_9 - or C_{10} -monoterpene moiety isolated from the plants of families Apocynaceae, Rubiaceae and Loganiaceae are extracted from the literature and summarized in tables. For this purpose we included the considerations about their structural features as well as their absolute configuration. For the absolute configuration, if it is known, we used the letters α or β depending on the configuration at C(15) (scheme 2). The huge number of alkaloids (3450 isolations and 1100 alkaloids) have been classified in eight different skeleton types (corynanthean (C)-, vincosan (D)-, vallesiachotaman (V)-, strychnan (S)-, aspidospermatan (A)-, eburnan (E)-, plumeran (P)-, and ibogan (J)-types). In this way, we have been able to demonstrate that those skeleton types with a non-rearranged secologanin (ae) skeleton constituting the C_{10} -monoterpene moiety have the same absolute configuration as the secologanin itself. On the contrary, the alkaloid structures with a rearranged secologanin part (E, P, J) occur, as expected, with an opposite configuration.

The subdivision of each of the eight skeleton types has been undertaken according to the increasing "chemical complexity" compared with the respective main skeleton. The comparison of the eight skeleton types and their occurrence in plant

families allowed us the following arguments : the skeleton types with a rearranged secologanin moiety (E, P, J-types) do exclusively occur in the subfamily Plumerioideae of Apocynaceae. The occurrence of the alkaloids of A- and S-type are restricted to Loganiaceae and Apocynaceae. On the other hand, alkaloids of C-, D- and V-types have been detected in all of the three plant families. Another detailed examination of the different C-skeleton variations gives rise to the evidence that only structurally simpler alkaloids do occur in all of the three plant families. With increasing "chemical complexity", their occurrence in special families, subfamilies tribes and genera becomes more specific.

As a result of this kind of investigations, chemotaxonomic considerations can be established for botanical differentiations and evolution of the plant families. The botanical classification and relationships, as demonstrated in scheme 19, can be regarded as a summary of this study.

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Curriculum vitae

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